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Collins' Advanced Science Series.

A MANUAL

OF

METALLURGY.

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VOL. II.

COPPER, LEAD, ZINC, MERCURY, SILVER, GOLD, NICKEL,
COBALT, AND ALUMINIUM.

ILLUSTRATED BY 67 ENGRAVINGS.



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P R E F A C E.

THE aim of the author, in the present as in the preceding volume of this work, has been to present to the reader an *accurate*, *useful*, and as *comprehensive* an account as space would permit, of the typical and more generally employed methods pursued in the extraction of the useful metals from their ores; and to offer such explanations as are generally received of the scientific principles upon which the several operations are based and metallurgical phenomena depend, without attempting to enter at any considerable length upon a description of the multifarious technical details of the several processes, or the details of their numerous modifications, as required by local circumstances, etc. But for such accounts, as also for the records of much original investigation bearing upon the numerous principles involved in the range of metallurgical science, the author would refer the student to the more elaborate treatises upon the subject, and for the study of which, it is hoped, the perusal of these volumes may have been an advantageous preliminary.

The subject of *assaying*, though forming an important branch of metallurgical science, does not permit of any useful *résumé* being effected within the space that could be devoted to it in the present work, and it has accordingly not been touched upon; while, for like reasons, the consideration of the details of the numerous mechanical appliances of every

day use in metallurgical establishments, such as engines, fans, rolling mills, etc., and which belong more properly to the sphere of Applied Mechanics, has been avoided.

The modern chemical notation, nomenclature, and atomic weights introduced in the first volume have been continued throughout the present part.

The author has great pleasure in again acknowledging the assistance he has derived from such standard works as those of Dr. Percy, of Rivot's *Principes Généraux du Traitement des Minerais Métalliques*, 1872; Kerl's *Handbuch der Metallurgischen Hüttenkunde*; Phillips' *Metallurgy of Gold and Silver*; Plattner's *Vorlesungen über Allgemeine Hüttenkunde*; various papers distributed throughout the proceedings of the different learned societies, and articles in the various scientific journals.

W. H. G.

MANCHESTER; April 1875.

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M E T A L L U R G Y.

CHAPTER I.

COPPER.

THE newly fractured surface of copper is of a pale or salmon-red colour, possessed of a silky lustre, and presenting a very finely granular, or, after hammering, finely fibrous appearance; but the presence of small quantities of impurities materially influence the colour, lustre, and kind of fracture, as will be specially noted when speaking of *tough-cake* and *dry copper*. Copper has, when heated and rubbed, a peculiar, somewhat disagreeable odour, and possesses a peculiar faint nauseous metallic taste. This metal is moderately hard, is elastic, and sonorous; it is *malleable*, *ductile*, and *tenacious* in a high degree; in the last-mentioned respect standing below iron, but above gold, silver,* etc. Copper can be hammered or rolled into thin sheets, or drawn into moderately fine wire; but in these operations the metal is hardened, and requires frequent annealing or softening during the processes, which softening is effected by heating to redness, and either subsequently allowing it to cool slowly, or quenching it in cold water; the effect of heating and sudden cooling thus producing the reverse effect on copper to that which occurs when steel is similarly treated.

The *specific gravity* of copper free from cavities is from 8.91 to 8.95; but the metal, as cooled after fusion in contact with the atmosphere, is more or less vesicular, and its density is accordingly reduced; while by hammering up to a certain point its density may be increased; as also by the application

* Vol. I., p. 11.

of pressure to the metal while in its fluid state.* As a conductor of heat and electricity, it is possessed of great power, ranking next to silver; but its electrical conductivity is materially impaired by the presence of only small proportions of impurities, especially of red oxide of copper (Cu_2O), of arsenic, or of phosphorus. The *specific heat* of copper is .09515, between 0° and $100^{\circ}\text{C}.$, and its *linear dilatation*, according to Troughton, is .00001918 for $1^{\circ}\text{C}.$ Copper melts at a temperature of about $1091^{\circ}\text{C}.$ ($1996^{\circ}\text{F}.$), or above the fusing point of silver ($1000^{\circ}\text{C}.$), and below that of gold ($1200^{\circ}\text{C}.$). It expands on solidification, and is not sensibly volatilised at ordinary furnace temperatures, but may be volatilised before the oxyhydrogen blowpipe: if heated to a temperature just below its melting point, it becomes brittle and coarsely fibrous on fracture. When cast in an open mould, the surface of the cast ingot does not present any sensible longitudinal ridge or furrow on its upper surface, like that presented by an ingot of *overpoled* or *underpoled* copper respectively. Copper crystallises in the regular system as cubes, octahedra, rhombic dodecahedrons, etc.

At ordinary temperatures this metal is not altered by exposure to dry air, but at a red heat it oxidises rapidly; while at ordinary temperatures in moist air, in the presence of carbonic anhydride, it becomes rapidly coated with a green layer or scale of carbonate of copper "verdigris." At a high temperature, copper decomposes the vapour of water. Cold hydrochloric acid is without action upon this metal; but, when boiled with it, hydrogen is evolved, and cuprous chloride (Cu_2Cl_2) remains in solution. Copper assumes the passive condition when immersed in very strong nitric acid (specific gravity 1.52); but on slight dilution a violent reaction is set up with evolution of nitric oxide ($8HNO_3 + 3Cu = 3(Cu_2NO_3) + 4H_2O + N_2O_2$). Dilute or strong sulphuric acid is without action upon the metal at ordinary temperatures; but on the application of heat, sulphurous anhydride (SO_2) is evolved, and cupric sulphate, with a little free sulphur and cuprous

* In an experiment made by the author, a specimen of best selected copper, cast as an ingot in an open mould, indicated a specific gravity of 8.835, while a sample of the same metal, melted and subjected to pressure while in its fluid state, had a specific gravity of 8.876.

sulphide, remain in the apparatus. Iron, either as wrought or cast-iron, precipitates metallic copper from its solutions, but the action of cast-iron is more slow than that of wrought iron. Copper in its molten state can dissolve and retain on solidification a certain amount of the red oxide (Cu_2O); and pigs of metal thus holding cuprous oxide in solution present a *longitudinal furrow* or *depression* along their upper surface, while the metal, known then as *dry copper*, breaks off a purplish red colour, duller in lustre and void of the fibrous structure evidenced in pure copper, while its malleability is much impaired, both in the hot and cold state. The chemical symbol of copper is Cu, and its atomic weight 63·5.

1. **Impurities in Commercial Copper.**—The usual impurities occurring in the copper of commerce are *iron*, *arsenic*, and *silver*, in small quantities almost invariably; *bismuth* very frequently, except in Russian and Australian specimens; *tin*, *antimony*, and *sulphur* occasionally, and *lead* almost invariably in sheet or bolt copper, but not in cake copper, with *nickel*, *cobalt*, and *gold* less frequently. The variety known in commerce as *best selected*, is very nearly pure; while *tile copper* and *tough-cake* usually contain traces of arsenic, iron, sulphur, tin, nickel, etc.

The effect of *iron* is to render the copper harder and paler in colour; *sulphur* and *antimony* likewise harden copper, make it greyer in colour, and impair its malleability and tenacity. Copper containing 10 oz. of antimony per ton is stated by Dr. Miller to be quite unfit for use in the preparation of brass intended for rolling. *Arsenic* in small quantities hardens the metal, but does not impair its malleability to the same extent as antimony; while the presence of *bismuth* deteriorates the toughness of the metal, and produces a red-short copper. Red oxide of copper (Cu_2O) renders the metal both red and cold-short. Small quantities of lead are occasionally added to copper intended for rolling, but the addition of only small quantities (1 to 2 per cent.) of this metal renders copper unfit for the manufacture of brass plate and wire.

2. **Varieties of Commercial Copper.**—*Cement copper* is the name applied to the almost chemically pure variety of copper obtained by the precipitation process as conducted at Anglesea, Hungary, etc., described under "Copper Smelting."

Rosette and **Japan Copper** are commercial varieties of copper, the surface of which presents a peculiar red colour, due to a coating of oxide of copper formed by throwing water upon the surface of the metal while still in a heated state. The first variety produced at Chessy in France, in the Hartz, in Sweden, China, etc., is obtained in thin plates or discs, by projecting water upon the surface of the cake of fluid metal, and removing the crust so formed as quickly as solidified, proceeding thus until the whole of the copper is removed in the form of thin discs, which are then immersed in water as quickly as possible to prevent their further oxidation. This variety contains a considerable amount of the red oxide of copper (Cu_2O), and has a dull red-short fracture; it requires refining before it can be hammered or rolled. The Japanese variety, instead of forming discs, occurs as small ingots, each weighing about 6 oz., and strongly coloured of a purplish-red tint by throwing them into water as quickly as solidified. It is made for exportation to the East Indies.

Bean-shot and **Feathered-shot** copper are varieties obtained in the form of small globules and flakes respectively, convenient for the brass-founders' use, and prepared by running the melted copper through a perforated ladle into hot water for the production of bean-shot; or into cold water if feathered-shot be desired.

Commercial copper possessing its most perfect malleability is called *tough-pitch* copper or *tough-cake*, since in this state it is cast into flat rectangular cakes or slabs convenient for rolling or hammering into sheets; such cakes weighing about 140 lbs., and measuring about 19 in. by $12\frac{1}{2}$ in., and $1\frac{3}{4}$ in. in thickness.

"**Best selected**" is the name applied to the purer varieties of commercial copper, as required in the manufacture of brass for sheets and wire, such metal being especially freed from tin, arsenic, iron, and sulphur. The special modification in the smelting operations for its production are described on page 44; and in one modification of the selecting process, the impurities above noted are concentrated in the lower portions of the selected pigs; when the less pure copper, prepared from these detached lower portions, is known in the market as, "*bottoms*," or when cast in tile-shaped pigs

of the same size as tough-cake, though usually only about $\frac{1}{2}$ inch in thickness, as "*tile copper*."

Russian Copper generally contains traces of iron, but in other respects is exceedingly pure. The *native* metal occurring in the neighbourhood of Lake Superior is usually very free from impurity, but occasional specimens yield .0003 per cent. of silver.

Chilian copper, as imported into this country, occurs in the form of bars, weighing about 200 lbs. each, having a composition analogous to the Welsh "pimple" or "blister copper," and which accordingly requires to be refined, or may be both roasted and refined before it is ready for the market.

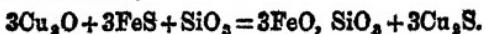
3. Copper and Oxygen.—The combinations of copper and oxygen of metallurgical importance are cuprous oxide, known also as the suboxide or dioxide of copper (Cu_2O), and cupric or protoxide of copper (CuO), both of which are reduced to the metallic state by heating to redness with carbon or carbonaceous matters, hydrogen, carbonic oxide, or metallic iron.

Cuprous oxide (Cu_2O) constitutes the dark-grey or black-looking scale, formed when sheet copper is heated to redness in contact with the air, as in the annealing of plates during the process of rolling sheet copper; or the same oxide results when copper and cupric oxide (CuO) are heated together. As prepared by these methods, and obtained in thin laminæ, it transmits a ruby-red light, and melts at a temperature somewhat below whiteness; but as prepared by more purely chemical methods, as an ingredient for communicating a ruby-red colour to glass, it occurs finely divided, and of a purer crimson colour. This oxide is soluble in an excess of hydrochloric acid with the formation of cuprous chloride, which latter is decomposed by water, sulphuric, phosphoric, or acetic acids, with the formation of cupric salts and the precipitation of metallic copper. Cuprous oxide occurs native as *copper bloom*, etc., as will be noted under copper ores, etc. Silicates of this oxide may be obtained by heating cupric oxide (CuO) and fine sand, with sufficient metallic copper to reduce the cupric to cuprous oxide. Cuprous oxide (Cu_2O), heated with ferrous sulphide and silica in certain proportions, yields a

slag of ferrous silicate, whilst the copper is separated as sulphide, thus—



or in the old notation,



Cupric oxide (CuO) is produced when the last oxide is reduced to powder and heated to redness in a muffle or other oxidising atmosphere; but in the massive form, cuprous oxide is not sensibly raised in oxidation by this treatment. Cupric or black oxide of copper, when heated to near the melting point of copper, liberates oxygen, and a mixture of cuprous and cupric oxide remains behind. If silica be heated with this oxide, Dr. Percy states that oxygen is liberated, and a silicate of the red or cuprous oxide is obtained.

Both oxides combine readily with boracic acid with the production of readily fusible borates.

4. Copper and Sulphur.—These elements have strong affinities for each other, simple trituration of the two, when in a finely divided state, sufficing to effect their combination; copper burns in the vapour of sulphur, and when copper and sulphur are heated to redness combination ensues, with incandescence of the mass, and the production of a black or lead-grey, compact, readily fusible, semi-metallic looking body, constituting cuprous sulphide (Cu_2S). There are six compounds of copper and sulphur tabulated, but only cuprous and cupric sulphides are of any metallurgical importance; the former constitutes the minerals Copper-glance and Redruthite, while the latter occurs native as Indigo copper.

Cuprous sulphide (Cu_2S), called also disulphide of copper, when heated out of contact with the air, does not suffer decomposition; but with access of air, combustion of the sulphide ensues, with the evolution of sulphurous anhydride (SO_2) and the production of cupric oxide; or, if the temperature attained be insufficient to decompose any cupric sulphate that is formed, then the residue will consist of a mixture of the latter with cuprous and cupric oxides and cuprous sulphide. Heated to redness in a current of aqueous vapour and but little decomposition ensues; but if the temperature be raised, sulphuretted hydrogen escapes and cuprous oxide (Cu_2O)

remains; and at a white heat the copper is reduced to the metallic state, with the escape of hydrogen, sulphuretted hydrogen, and sublimed sulphur (Regnault). Cuprous sulphide is imperfectly decomposed by heating with metallic iron, with the production of copper containing iron and a double sulphide or regulus of copper and iron. This sulphide, heated with the proper proportions of cupric oxide, or of cuprous oxide, cupric oxide, and cupric sulphate, yields sulphurous anhydride and metallic copper, or these bodies, along with cuprous oxide (Cu_2O) and sulphide, according as the oxygen or sulphur is in excess in the mixture. There is but little reaction when disulphide of copper is heated in a current of hydrogen; but it suffers *partial* reduction when heated to a high temperature with charcoal, lead, or zinc; or on fusion with carbonate of soda and charcoal, or with charcoal and baryta or lime. Cuprous sulphide is soluble only with difficulty in boiling hydrochloric acid.

Sulphate of copper or *cupric sulphate* ($CuSO_4 + 5H_2O$), called also "blue vitriol," is obtained when copper pyrites is roasted with free access of air, or when copper scale is dissolved in sulphuric acid. This salt is held in solution by the water flowing through many copper mines, from which waters the copper is frequently extracted by the method of precipitation with iron. When heated to redness, this salt loses its water of crystallization, with the production of a white powder, whilst at a higher temperature it suffers decomposition, leaving a residue of oxide of copper.

5. Copper and Carbon.—Copper does not appear to form any definite compound with carbon, but if ordinary commercial copper be melted under charcoal and then recast, it is found to have acquired the qualities of *overpoled* copper, i.e., it is brittle at a red heat, or no longer capable of being rolled into thin sheets; "best selected" or electrotype copper does not however suffer by this treatment, and Percy considers it probable that the effect is not due therefore to any combination with carbon, but that ordinary copper retains in its composition a certain amount of the red oxide (Cu_2O), which acts as an antidote or corrective to the other impurities, and is essential to the malleability of commercial copper; while by treatment with carbonaceous matters, the oxide is reduced to the

metallic state and brittleness of the product ensues; whereas in pure copper, as the electro-deposited metal, cuprous oxide and the other impurities do not exist, and its fusion under charcoal is not attended with the same result. The effect of fusing commercial copper under carbonaceous matters is the same as *overpoling* in the refining of copper, while an excess of cuprous oxide in the metal corresponds to the *underpoled* condition of copper.

6. Copper and Phosphorus.—These elements combine directly under the influence of heat, or by heating copper with bone-earth and charcoal. By introducing pieces of phosphorus into melted copper, about 11 per cent. of the former may be combined with the copper, when the product is grey or approaching to whiteness in colour, is very hard and brittle at ordinary temperatures; but, with smaller quantities of phosphorus, the hardness and fusibility of the copper are increased, the metal casts more soundly, contracts on solidification, and resists the action of sea water better than ordinary copper, from which quality it has been proposed as a material for ships' sheathing; this phosphorised copper may be rolled cold, but is brittle when hot, even when containing only .5 per cent of phosphorus.

7. Copper and Silicon.—A combination of these elements results when potassic silico-fluoride, sodium, and copper turnings are melted together. The effect of silicon, however, is to increase the hardness and impair the malleability of the metal. With about 4·5 per cent. of silicon, the compound has a bronze colour; while with 12 per cent. of this element the resulting body is white in colour and very hard.

Silicates of copper occur native as the mineral *chrysocolla*, occurring along with other copper ores in Cornwall, Hungary, Norway, etc.

8. Alloys of Copper.—Copper unites easily with most other metals, and forms the basis of a large number of important alloys; with zinc it forms the varieties of *brass*, *tombac*, *Muntz's metal*, *Mosaic gold*, *pinchbeck*, *Manheim gold*, *prince's metal*, described in the chapter on Zinc; with tin it forms the alloys known as *bronze*, *gun* and *bell metal*, described in Part I.

Copper and arsenic yield an alloy of almost silver white-

ness, sometimes used for dial-plates, scales, etc., while copper and *tin*, in the proportion of about 64 parts of the former to 32 of the latter, with a small proportion of arsenic, yield *speculum metal*; and, alloyed with gold and silver, copper enters into the composition of the gold and silver coinage of this and other countries. The British silver coinage, consisting of 925 parts of silver with 75 of copper; the French, of 900 parts of silver to 100 parts of copper; while the Prussian and German coinage are much poorer in the noble metals. Our gold coinage consists of 916·6 parts of gold with 83·4 of copper; the effect of copper in this quantity is to harden the gold and silver without materially affecting their colour or malleability; but with larger quantities of copper the gold becomes more or less brittle.

An alloy of 9 parts of copper with 1 of *aluminum*, known as "aluminum bronze," is used in the manufacture of ornamental articles in imitation of gold. The alloy is not so heavy, but is harder than gold, and though not rapidly acted upon by the atmosphere, yet it does, after a lengthened exposure, become sensibly tarnished.

Copper and manganese yield alloys having the appearance and general characters of German silver (Dr. Percy).* The alloys of these two metals, containing from 5 to 30 per cent. of manganese, are described as malleable and ductile, while possessing considerable tenacity;† can be rolled readily and are highly elastic in the cold, but become brittle when heated. When zinc is added to this alloy, it possesses many of the qualities of German silver, it can be rolled when heated, but it is wanting in many of the best qualities of the last-mentioned alloy.

German silver is an alloy of copper, zinc, and nickel, described in Chapter VII. of the present volume.

9. **Phosphor Bronze.**—By the addition of 5 parts of *phosphorus* to 1000 of copper, the hardness and tenacity of the metal are increased, while the presence of phosphorus in larger proportions renders the metal brittle, p. 16. It further increases its fusibility, and the phosphorised copper also casts sounder, that is, freer from air-holes than does pure copper.

* *Chem. News*, xxvii., 249.

† *Proceedings of the British Association*, 1870.

While the presence of *minute* proportions, almost traces, of phosphorus in the alloy of copper and tin, known as bronze, is attended with the production of a body known as "*phosphor bronze*," for which the inventors claim many important and remarkable chemical and mechanical qualities.* Bronze thus combined with an exceedingly small proportion of phosphorus, the exact proportion being stated to vary with the proportion of tin contained in the alloy, is somewhat paler in colour than the ordinary bronze. It can be rolled and hammered into thin sheets with great ease, is possessed of considerable tenacity, specimens submitted for testing having withstood a tensile strain greatly in excess of that afforded by copper or bronze, and ranging as high as 74,966 lbs., or over 33 tons per square inch, thus attaining to the strength of mild steel; while after wire-drawing, the above figures have been much exceeded. The density and elasticity of the bronze are also considerably increased by the addition; while the phosphor bronze, when melted, has considerable fluidity, filling the smaller details of moulds perfectly, and yielding very clean castings. Its powers to resist atmospheric oxidation, or corrosion from the action of sea water, are stated to be much superior to bronze; and it is further stated that it is capable of withstanding considerable wear and tear while exposed to the action of high pressure steam.

The application of phosphor bronze, as a material for the construction of twyters, has been already noted under "iron;" and the patentees claim for it very superior merit over cast-iron, etc., for the construction of wheels and pinions in rolling mills, etc., which are subject to sudden and violent shocks. It has likewise been proposed as a material for the construction of ordnance, etc.

The process for the preparation of phosphor bronze, which has been invented by Messrs. Montefiore and Künzel, is kept secret, though it is understood that they first prepare a rich compound of phosphorus and tin,† which is then employed for addition to the copper, instead of adding the phosphorus directly to the bulk of the copper and tin.

It has been proposed that the production of such material

* *Journal of the Iron and Steel Institute.* 1873. Part II.

† *Engineer.* Feb. 1872.

results, by the presence of almost infinitesimal proportions of phosphorus, may be due to the superior affinity of the latter for oxygen, whereby it promotes a more intimate union between the particles of copper and tin in the bronze, by preventing the oxidation of the tin, which otherwise always occurs during the melting of the alloy; while that, if a greater proportion of phosphorus be added than is required for this purpose, its effect is to still further and unduly harden the alloy for all but special applications.

10. **Ores of Copper.**—Copper occurs very abundantly, and in a variety of forms; but many minerals containing it are much too poor in copper to allow of its profitable extraction, or do not occur in sufficient abundance to permit of their classification as ores of copper, and such accordingly will not be noted in this place. The ores of copper occur in rocks of almost all ages, but most abundantly in the Lias and Permian formations, the *lodes* of Cornwall occurring in Permian and older rocks, and the ores are most frequently accompanied by *iron pyrites* and *quartz*, while in some Cornish mines *fluor spar* occurs largely. The metal occurs in the *native* or metallic state, also as *oxide*, *sulphide*, *carbonate*, *chloride*, *sulphate*, *phosphate*, and *silicate*, etc., of copper.

Native copper is found in isolated masses, sometimes of considerable size, in thin laminæ, or in filiform pieces, and the *copper sand*, or *barilla* occurring in Chili, consists of metallic copper in small grains, mixed with quartz; occasionally a mass of copper ore will consist of carbonate of copper on the outside, enveloping an inner layer of red oxide, itself enclosing an inner nucleus of metallic copper. Native copper is ductile, malleable, and exceedingly tough: it is usually very pure, but is often accompanied by small quantities of silver; in Chilian varieties the latter occasionally amounting to 7 or 8 per cent. of the metal. The chief localities of its occurrence in quantity are the United States, near Lake Superior, Brazil, Chili, Peru, Siberia, Faroe Isles, in some of the Cornish mines, near Redruth, also in North Wales, and in smaller quantities not unfrequently along with other copper ores in the various localities of their occurrence.

The *red oxide* or *cuprite* (Cu_2O) contains, when pure, 88.78

per cent. of copper, and is found massive or granular; frequently iron-grey on the surface, but always affording its characteristic reddish-brown streak. It occurs at Huel Gordan and other Cornish mines, in New Jersey and the district of Lake Superior, in South America, but most abundantly in Australia.

The *black oxide* (CuO) contains, when pure, 79.8 per cent. of copper, but it is frequently very impure. It occurs in Lake Superior, in Saxony, Chili, and at the Burra Burra mines of Australia.

Green carbonate of copper or *Malachite* ($\text{CuCO}_3 + \text{CuO}, \text{H}_2\text{O}$) contains 57 per cent. of copper, and is distinguished by its fine emerald-green colour, with a lustre inclining to resinous, and a streak of a somewhat paler tint than the mineral in the mass. It occurs massive in the Ural mountains, in South Australia, Siberia, the United States, and South America, and incrusting other ores in most copper mines.

Azurite, *Chessylite*, or blue carbonate of copper ($2\text{CuCO}_3 + \text{CuO}, \text{H}_2\text{O}$), contains 55.16 per cent. of copper, and occurs along with the green carbonate of copper in Australia, as also in Cornwall, Chessy in France, and in the United States.

Copper pyrites, or *yellow copper ore* ($\text{Cu}_2\text{S}, \text{Fe}_2\text{S}_3$), forms the ore from which about five-sixths of the copper produced in Great Britain is obtained, its formula shows it to contain, if pure, 34.81 per cent. of copper; but its average yield as prepared for sale is only from 4 to 12 per cent., or usually 7 to 8 per cent. of copper. This ore is of a brass-yellow colour, distinguished from iron pyrites, which it resembles, by its inferior hardness; it is found associated with quartz, gneiss, and clay-slate, and occurs in large quantities in Cornwall and Devon, accompanied by *grey copper ore*, *galena*, *blendes*, *copper glance*, *tin stone*, etc.; it occurs also in Sweden, Saxony, Cuba, South America, the United States, Australia, and elsewhere.

Vitreous or *grey sulphide* of copper, *Copper-glance* or *Red-ruthite* (Cu_2S), and *purple copper*, are sulphides of copper occurring largely in Cornwall and elsewhere, associated with haematite iron ores, and containing variable proportions of sulphide of iron: a variety of the purple ore occurs in the cupiferous shale of Mansfeld, in Saxony.

Grey copper ore, fahlerz, or fahl-ore, is a steel-grey or iron-black, brittle mineral, occurring both massive and crystallised in cubic forms. It is a cuprous sulphide, in which the copper is replaced more or less by iron, zinc, silver, and mercury, along with variable proportions of the sulphides of antimony and arsenic. The argentiferous fahl-ore contains occasionally 30 per cent. of silver, and not more than 15 per cent. of copper; whilst others contain as much as 48 per cent. of copper, with but small proportions of silver. Gold is also sometimes a constituent of this ore. Fahl-ore occurs in Cornwall, Norway, Sweden, Saxony, Hungary, the Hartz, Mexico, etc.

Chrysocolla, a hydrated silicate of copper; and *Atacamite*, a hydrated oxychloride of copper, are sometimes employed for the extraction of the metal. The former occurs accompanying other copper ores in Cornwall, Saxony, Nova Scotia, Chili, Australia, and Lake Superior; and the latter is also found in Chili, Australia, Saxony, etc.

The ores imported to Swansca from Cuba are known as *Cobre ores*.

Cupric sulphate occurs in considerable proportion in the waters issuing from certain copper mines, as those of Amlwch, Wicklow, the Rio Tinto, and Tharsis mines of Spain, etc.

11. Ticketing and Standard.—The ore, after dressing by the miner, is sold to the smelter, at a sale or meeting known as a *ticketing*, prior to which meeting the smelter receives a sample of the various ores for assay, and according to the *produce* or yield of the ore, he determines upon the price he will give for it; and at the periodical meeting for their sale, the smelters each deposit a slip of paper containing the price per ton of 21 cwt. which he offers, when the highest offer thus made obtains the lot, or *parcel*, as it is called. The *standard* is the price per ton of the metal as calculated from this ticketing or purchase, estimated by adding to the price given per ton for the copper (as indicated by the assay of the ore), the cost of transport from the mine to the smelting works, together with a fixed sum representing the cost per ton of smelting an ore of the given *produce*. But the term obviously serves only as a comparison of the relative value of copper in the ore at different periods.

COPPER SMELTING.

The processes of copper smelting, and the furnaces employed, vary very much with the nature of the ore, and the facilities of the locality for supplying coal and fire-clay, etc., for the construction of the furnaces. Thus, for the reduction of carbonates and oxides of copper occurring in a gangue of clay, and notable by the absence of sulphides, the ores are smelted by simple treatment with coke and a flux of lime; while ores like the last, but containing copper pyrites in addition, are smelted in the Ural districts in blast furnaces using wood as the fuel, when the product is an impure metal known as *black copper*, requiring further purification. But by far the most important process of copper smelting is that practised at Swansea, and known as the *Welsh process*, in which reverberatory furnaces are wholly employed.

The methods employed for the reduction or smelting of copper may thus be placed under two classes: (1) Smelting or reduction in the *dry way*, which includes the English method of smelting in *reverberatory furnaces*, and the Continental method of smelting in *blast furnaces*; and (2) the extraction of copper in the *wet way*, in which cuprous solutions are decomposed by iron with the precipitation of metallic copper; or if sulphides be the subject of treatment, they are first converted into sulphates or chlorides, and these compounds subsequently decomposed by iron, calcic sulphide, or lime.

SMELTING IN REVERBERATORY FURNACES; OR "WELSH PROCESS" OF COPPER SMELTING.

The ore smelted in the Welsh method is chiefly copper pyrites, but other and richer ores, consisting of cuprous oxides and carbonates with native copper, etc., are imported for mixing with these, and for introduction at various stages of the process; and upon the mixture of ores employed depends the number of operations involved in the process. As conducted with the minimum number of operations, it consists from the first calcination to the refining of six distinct operations; but this can only be effected

when ores, consisting of carbonate and oxide of copper, as Australian ores, are available for introduction into the furnace charge at the proper stages.

The smelting charge, consisting of copper pyrites with oxides and carbonates of copper, and a gangue essentially silicious, is mixed so as to obtain a mixture yielding from 8 to 13 per cent. of copper; for if poorer than this lower figure, the mixture is unprofitably poor from the large proportion of fuel required per ton of copper produced; and if above the higher, a loss of copper occurs in the slags. The gangue of the mixture should also be so regulated as to fuse readily, while yet yielding a slag free from copper; or, in other words, the proportions of lime, ferrous oxide, and silicious matters present, should be apportioned so as to afford the desired fusibility.

If the ore consist entirely of sulphides, then the smelting will involve eight, ten, or even twelve operations, consisting of alternate *calcinations* and *fusions*, during which arsenic, sulphur, and volatile matters are more or less completely expelled in the various calcinations, and the iron partially eliminated at each fusion in combination with silica, constituting the slag; and thereby the copper becomes more concentrated in each succeeding regulus or matt derived from the successive fusions.

The Welsh process, as conducted in six stages, involves the following operations—

1. *Calcination* of the ore with access of air, whereby arsenic and volatile matters, as carbonic acid, water, and fluorine compounds, are expelled, as also a portion of the sulphur, in the form of sulphurous anhydride (SO_2), while the iron is oxidized, so that, in addition to earthy matters, the calcined product contains iron, copper, silicon, oxygen, and sulphur, which are the chief elements concerned in the succeeding stages.

2. *Fusion*, or melting of the last product with "metal slag," the product of the fourth operation; and sometimes an addition is made of small quantities of ores, as oxides and carbonates along with fluor-spar. The products are a regulus which is granulated by tapping out into water, or is cast into pigs, and subsequently crushed between rollers, and known as "granulated or crushed coarse-metal," containing

from 30 to 35 per cent. of metallic copper; and "ore-furnace slag," which should not contain more than 1 per cent. of copper, when it is usually thrown away.

3. *Calcination* of the "granulated coarse-metal," by which a further portion of the sulphur escapes as sulphurous anhydride and sulphuric acid. The product consisting essentially of cuprous sulphide, oxide of iron, and unchanged ferrous sulphide, is known as "calcined coarse-metal."

4. The product of the last operation is melted with *roaster* and *refinery slags*, along with oxidized ores as oxide and carbonate of copper, whereby a reaction ensues between the oxidized compounds of copper and the ferrous sulphide, by which the iron is converted into oxide, which combining with silica is removed as "metal slag," this latter containing also about 2 per cent. of copper; whilst the bulk of the copper is concentrated in a rich regulus or matt, varying in its physical qualities, but consisting essentially of sulphide of copper, and containing from 75 per cent. to 80 per cent. of copper, constituting *white, blue, fine or pimple metal*, according as the addition of oxidized bodies was *sufficient, insufficient, or in excess* of that required for the oxidation of the iron present in the coarse-metal.

5. In this the *roasting* process, the pigs of *fine metal* from the last stage are again calcined at a temperature below the melting point of the metal, by which treatment oxides of copper and iron are produced; upon which the mass is melted and a vigorous reaction ensues between the sulphide and oxide of copper, whereby metallic copper is separated, sulphurous anhydride escapes, and at the same time the antimony, arsenic, iron, silicon, cobalt, nickel, etc., are largely removed either as volatile compounds or as silicates in the slag. The products of this operation are "blister copper," containing about 95 per cent. of metallic copper and "roaster slag," rich in oxide of copper.

6. The last or *refining* operation involves two stages: the first has for its object the removal of any residue of sulphur and foreign metals from "blister copper" by the action of atmospheric air and the silicious matters of the furnace, with the production of *dry copper* and *refinery slag*, rich in copper; and the second stage, or *toughening* of the dry copper, consti-

tutes the operation known as *poling*, when the product is *tough-cake* or tough pitch copper.

As already noted, if a sufficient supply of oxidized compounds of copper are not at command, as required for the above cycle of operations, then one or more calcination and fusion intervenes between the fourth and fifth operation above noted.

The *metal* and *ore-furnace slag*, if they contain shots of *regulus*, are remelted for the separation of the metallic portion, and the regulus so obtained is added with the charges in the previous list of operations; but such smelting is not added in the general role, since it is only accessory and occasional, and is not performed upon the concentrated metalliferous product of a previous stage.

12. Calcination.—This process is conducted in large reverberatory furnaces, called "calciners." These have very low roofs, and are built in sizes to calcine from 3 to 7 tons of ore at each charge, while the parts which are exposed to the heat are built of fire-brick. In the accompanying figures of a *calciner*, calculated to roast from 3 to $3\frac{1}{2}$ tons of ore, the bed, formed of fire-bricks set in fire-clay, is from 16 to 20 feet in length, and from 12 to 14 feet in width; but in the larger furnaces the length is increased. The roof of the furnace (according to its size), has one, two, or three openings *b b*, for the introduction of the charge of ore, which has been previously broken into pieces of about the size of nuts. The openings *b b* are closed by fire-brick tiles during the working of the furnace, and over each aperture is suspended in an iron frame a *hopper* or *bin c c*, into which the charge is wheeled in barrows and subsequently allowed to fall on to the bed, the workman spreading it uniformly by the use of a *stirring rubble* inserted through the side or working doors *e e*, the triangular projections *d d* serving to prevent the ore from lodging inconveniently between the doors *e e*. In the bed of the furnace and in front of each door is a vertical opening *k k*, closed by a tile during the working of the calciner, but through which the calcined charge is raked at the close of the operation into the arched vault *m* below the furnace bed; which latter communicates with flues connected with the stack of the furnace, whereby any sulphurous or other noxious vapours

that may continue to be evolved during the cooling of the mass are conveyed away. The fireplace *f*, situated at one end of the calciner, is separated from the bed *A* by the fire-bridge *g*; and at the opposite end of the bed are flues *h h* which carry the vapours and products of combustion from

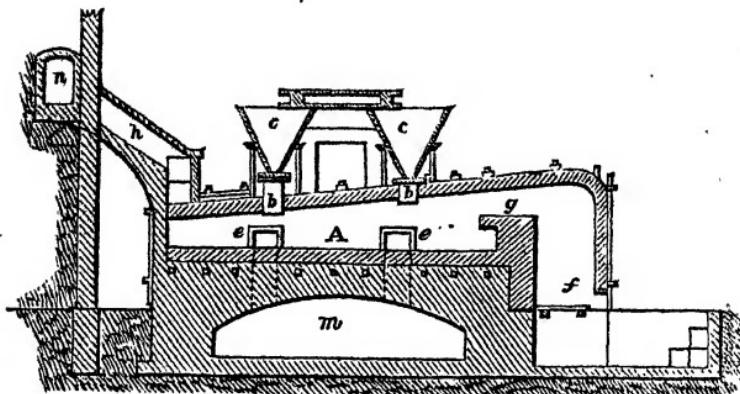


Fig. 1.—VERTICAL SECTION OF ORE-CALCINING FURNACE.

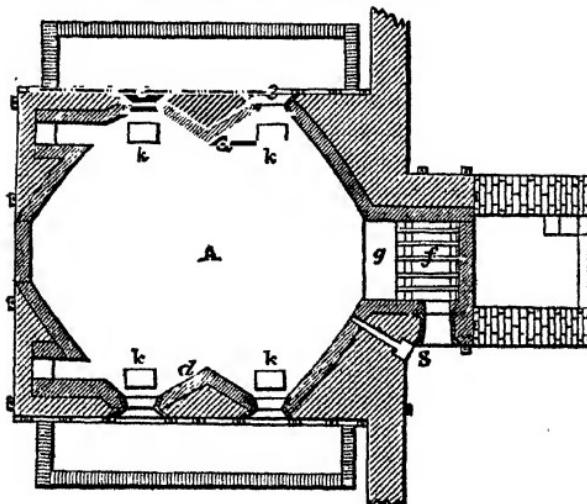


Fig. 2.—PLAN OF THE BED OF ORE-CALCINING FURNACE.

the furnace into a nearly horizontal flue *n*, into which a range of calciners deliver their gaseous products, and which, after traversing some distance, opens into a high stack. In the calciner, fig. 1, the fire-bridge is shown as built with an arch or curtain, reaching across, and projecting for a short distance over the bed of the furnace, serving thereby to prevent the ore near the bridge from being too strongly heated, and clotting or fusing into one mass. The fire-bars are of the ordinary description, resting on bearers, but are covered during the operation of calcination with a layer of clinker to prevent their otherwise rapid corrosion, produced by the intense heat generated in the combustion of the anthracite coal which is employed in Wales. The fire-grate is also rather deep, thereby holding a considerable charge of fuel, consisting of anthracite coal mixed with about one-fourth of its weight of bituminous coal, the latter being requisite to enable the anthracite to cake together, and yet retain the porosity necessary for its combustion; and also from the depth of fuel on the grate, the air in ascending from the bars through the mass of heated fuel, has its oxygen converted into carbonic oxide, which gas is then burnt on the bed of the furnace by the excess of air introduced through the opening *s* near the fire-bridge and other openings in the side doors of the furnace, thereby producing a long flame over the bed of the calciner, while maintaining a strongly oxidizing atmosphere above the heated ore in the chamber.

Fig. 3 is the plan of the bed of a *calciner* slightly different to the last, inasmuch as there is a passage *p* built through the fire-bridge, which communicates with the interior of the furnace by the openings *a a a*, which passage thus serves to cool the fire-bridge, and to supply a current of heated air for the combustion of the gases and oxidation of the ore. This plan is known as "Sheffield's" plan, from the name of its inventor. The bed also differs in having circular instead of triangular projections between the working doors of the calciner.

Calciners heated by gas, and provided with Siemens' regenerators, have been introduced into the Lancashire copper works with reported success.

In conducting the calcination, the charge of ore already

warmed by suspension in the hoppers above the roof of the heated furnace, is allowed to fall on to the heated bed of the calciner, and is then spread in a thin layer over its surface. The temperature is now gradually raised, and the ore stirred or moved about from time to time, care being taken that the temperature does not rise sufficiently high to fuse or clot the ore, of which there is the greater tendency in the earlier stages of the calcination. By thus heating the ore in an oxidizing atmosphere, about one-half of the sulphur along with arsenic and a portion of the iron contained in the ore are oxidized, with the production of sulphurous anhydride (SO_2) and sulphates, arsenious anhydride or acid (As_2O_3), and oxide of iron, respectively; the sulphurous and arsenious anhydride, along with smaller quantities of anhydrous sulphuric acid produced by the decomposition of the sulphates formed in the earlier stages, escaping along with the gaseous products of combustion into the flue, and so to the stack. The calcination is completed in from twelve to twenty-four hours, when the product, which is of a brownish-black colour, is raked into the vaults beneath the furnace bed, where it is cooled by throwing water upon it. The calcined ore contains cuprous sulphide (Cu_2S), with some cuprous oxide, along with oxide and sulphide of iron.

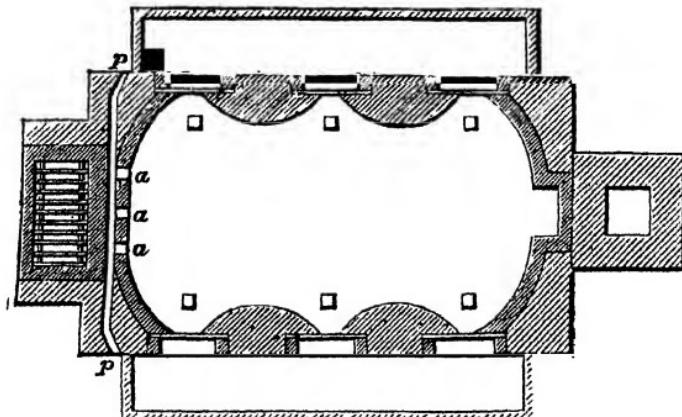


Fig. 3.—SHEFFIELD'S MODIFICATION OF CALCINER.

The gases from the ore calciner form a dense cloud over

the region of the smelting works, constituting what is known as the "copper smoke," and to prevent the escape of the deleterious portions of which, considerable expense has been entailed by the smelters in conducting the fumes or vapours along long flues into which water is injected, and finally delivering the gases at a considerable height into the atmosphere. The gases of the ore calciner consist chiefly of *nitrogen*, with *sulphurous* and *carbonic anhydrides*, along with about 9 per cent. of free oxygen.

Many attempts have been made to utilise the large amount of sulphur contained in pyritic ores in the manufacture of sulphuric acid; and numerous improvements in the calciners have been devised for this purpose, amongst which may be noted those proposed by Mr. Spence and M. Gerstenhöffer. Mr. Spence proposed a calciner with a bed heated from beneath and some 50 feet in length, on to which the ore was placed at the end most distant from the furnace, and gradually moved onwards towards the hottest end of the bed, a current of air being passed over the thin stratum of ore during the whole time of roasting, while the escaping sulphurous anhydride (SO_2) is carried to the ordinary sulphuric acid chamber.

The furnace or calciner of **M. Gerstenhoffer**, adopted for some time by Mr. Vivian, at Swansea, consists of a rectangular vertical chamber, across which are arranged rows of fire-clay bars about 2 feet 6 inches in length and triangular in section, these are arranged with their upper faces parallel with the top of the furnace, while the bars of each row in vertical height are placed beneath the spaces in the row above them, so that no two bars in succeeding rows are directly over one another. The ore or regulus is ground fine and introduced into a box or hopper on the top of the furnace, from which it is supplied to the furnace by grooved feed rollers placed in the top of the furnace above the uppermost row of bars; so that as the ore is fed in a continuous stream it falls on to the top row of bars, piles itself upon these, and gradually falls over on to the next series below, and so on, thus exposing a large surface for oxidation in the passage of the ore from the top towards the bottom; air being at the same time admitted through a series of apertures in the

front of the furnace, as also by a current driven in at the bottom of the calciner; while the gases escape by an opening at the top, from which they are conducted to the sulphuric acid chambers. The fireplace is at the bottom of the furnace, into which, at the commencement of the calcination, ignited fuel is introduced, and the fire maintained until the temperature of the furnace has been raised sufficiently high and the sulphur evolved from the ore is in ignition, after which the combustion of the sulphur is sufficient to continue the process. If the ore clots on the bars and does not fall over on to the series of bars beneath, a scraper can be inserted through the apertures in front for clearing away the obstruction.

13. **Fusion for Coarse-metal.**—The fusion of the calcined ore is effected like the last operation in a reverberatory furnace, but known as the "ore furnace," in which the bed is only about one-third of the size of that of the "calciner," and the proportion of fire-grate area to that of the bed is much increased in the ore furnace. The parts exposed to the action of the flame are built wholly of fire-brick.

The "ore furnace," figs. 4 and 5, consists of a more or less oval-shaped chamber *a*, bounded at the sides by low vertical walls, from which springs the low arched roof *b*, provided with an opening for the introduction of the charge from the hopper *c*. The bed is separated from the fire-grate by a hollow fire-bridge, while at the opposite end it communicates by a flue *d* with the stack *m*. At *f* is an opening, protected as shown by two cast-iron plates, and closed by a fire-clay slab or quarry, in which is a hole for the inspection of the interior of the furnace; and through which aperture the slags are withdrawn into the slag moulds situated immediately beneath. The fuel, consisting of *anthracite* with one-third of its weight of *bituminous* coal, is introduced through the opening *k*, not fitted with a door, but closed as in the puddling furnace, by the introduction of coal into the aperture *k*; and at *h* is the tap-hole, through which the melted coarse-metal is allowed to flow for *granulation* into a perforated tank, which is raised and lowered in a reservoir of water by a winch or crane at the side of the furnace. But in Lancashire, at St. Helen's, etc., as also in Swansea, according to the ores employed, instead of running the regulus from

the ore furnace into water for granulation, the metal is tapped directly into sand moulds, the pigs of metal from which are subsequently crushed under rollers prior to its calcination. The bed of the ore furnace is supported upon a brick arch running from the ash-pit for the whole length of the bed; upon this arch is built a bed of fire-brick, upon which is placed a depth of 10 or 12 inch of sand, which is strongly heated and consolidated by melting on its surface a small quantity of "metal slag," when a further but thinner layer of sand with slag is introduced in the same manner, and thus a comparatively impervious bottom is obtained; notwithstanding which, the old furnace bottoms still contain considerable quantities of copper. The surface of the bed is made to slope from all parts to the tap hole *h*, in front of which the metal collects in a kind of basin previous to tapping.

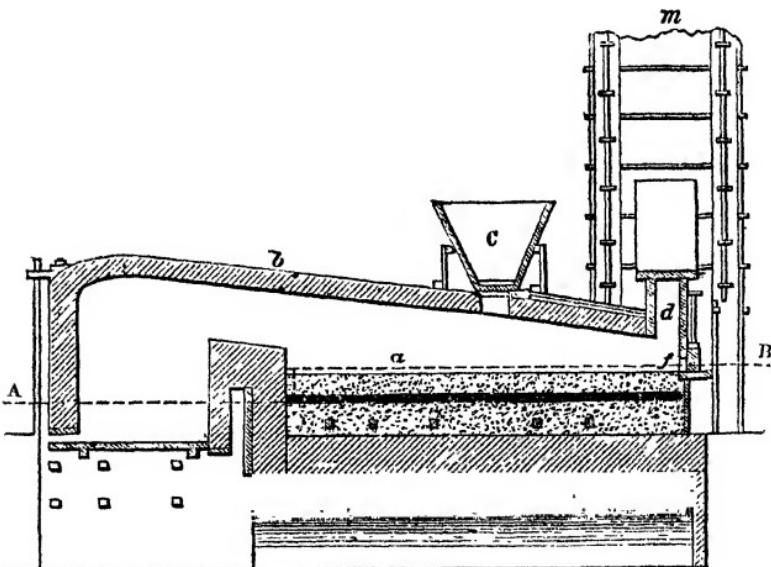


Fig. 4.—VERTICAL SECTION OF THE ORE FURNACE.

The charge of the furnace, weighing about 25 cwt., is made up of from 17 to 18 cwt. of *calcined ore*, about 3 cwt. of *raw ores* consisting of oxide and carbonate of copper when these

are available, along with 5 or 6 cwt. of *slags* from the fourth operation, the latter being introduced through the opening *f*, at the end of the furnace, and occasionally a little *fluor-spar* is added to increase the fluidity of the slags; for if the latter be either too thick or too fluid, more or less of the *regulus* is drawn over with it, as it is raked out through the opening *f*. In Lancashire, charges of 3 tons, consisting of 2 tons of calcined ore with 1 ton of oxidized ores, are frequently treated.

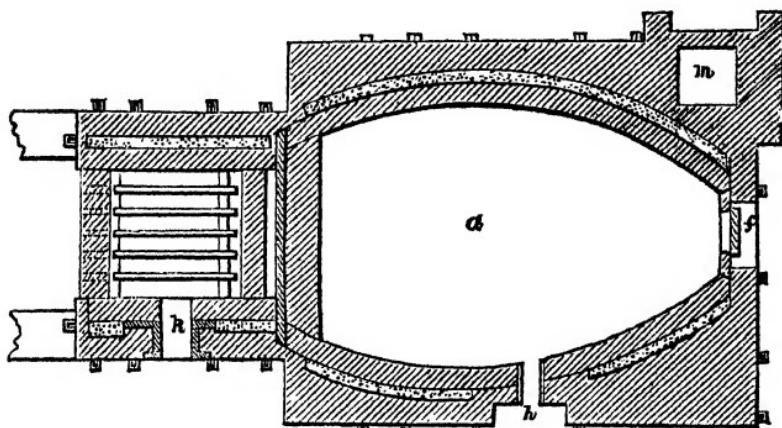


Fig. 5.—HORIZONTAL SECTION OF THE ORE FURNACE ON LINE AB.

The charge of ore, etc., having been introduced into the furnace by withdrawing a slide in the bottom of the hopper *c*, and spread evenly over the hearth, the openings are then made tight, and the temperature gradually raised. The mass is slowly melted, attended with ebullition from the escape of sulphurous anhydride (SO_2), and in about $3\frac{1}{2}$ hours the bath is in perfect fusion, when it is raked together by the workman, after which the temperature is raised still higher to favour the more perfect separation of the *regulus* or *matt* of *coarse-metal* from the slag. The whole operation is completed in about 5 hours, when the slag may be raked out into the sand moulds already mentioned (where the small quantity of regulus drawn out along with it collects in the lower portion of the blocks of slag, from which it is detached and added to the general yield of coarse-metal), while another charge is worked off before tapping

the furnace; or the regulus of coarse-metal, after raking out the slag, is at once tapped out, by withdrawing the stopping of clay and sand from the tap-hole, and either run, for granulation, into the perforated tank contained in the reservoir of water, or is cast in pigs to be subsequently crushed between rollers.

In the fusion for coarse-metal the oxides of copper produced in the calcination of the ore, as also those introduced in the state of raw ore, act upon the undecomposed ferrous sulphide, yielding by double decomposition cuprous sulphide and oxide of iron; and a further portion of the ferrous sulphide is oxidized by the oxygen of the air passing through the furnace, attended with the evolution of sulphurous anhydride and the production of oxide of iron, this last combining with the silica of the slags added to the charge, with the formation of a silicate of iron. While if sulphur be present in the calcined ore in insufficient amount to convert the whole of the copper into sulphide, then a portion of the metal separates as *blister copper*, forming a third and lowest stratum in the furnace, and at the same time the slags will contain oxide of copper as cuprous silicate.

As the result of the fusion in the "ore furnace" there is thus obtained a brittle, non-crystalline, more or less granular, vesicular and bronze-coloured regulus, known as "*coarse-metal*," which contains about 33 per cent. of metallic copper (or about the same proportion of copper as exists in copper pyrites). Besides cuprous sulphide, this regulus also contains ferrous sulphide, and smaller quantities of other metals. The coarse-metal is accompanied by a hard, brittle, porphyritic mass, constituting "*ore-furnace slag*," which consists essentially of ferrous silicate ($2\text{FeO}, \text{SiO}_2$), but contains also embedded angular pieces of quartz, shots of coarse-metal, and smaller quantities of other elements, as indicated by the accompanying analyses by Le Play. It is not desirable to concentrate the copper in this regulus or "*coarse-metal*" beyond about 35 per cent., nor to allow it to fall short of 30 per cent., these limits affording the best results in practice. The yield of coarse-metal is about 55 per cent. of the charge.

COMPOSITION OF COARSE-METAL.

Copper,	-	-	-	-	-	33.7
Iron,	-	-	-	-	-	33.6
Nickel, Cobalt, and Manganese,	-	-	-	-	-	1.0
Tin,	-	-	-	-	-	0.7
Arsenic,	-	-	-	-	-	0.3
Sulphur,	-	-	-	-	-	29.2
Slag mechanically mixed,	-	-	-	-	-	1.1
						99.6

COMPOSITION OF ORE-FURNACE SLAG.

Quartz in admixture,	-	-	-	-	-	30.5
Combined Silica,	-	-	-	-	-	30.0
Ferrous Oxide,	-	-	-	-	-	28.5
Alumina,	-	-	-	-	-	2.9
Lime,	-	-	-	-	-	2.0
Magnesia,	-	-	-	-	-	0.6
Oxides of Tin, Manganese, Nickel, and Cobalt,	-	-	-	-	-	1.4
Fluorine,	-	-	-	-	1.0	2.1
Calcium,	-	-	-	-	1.1	
Copper,	-	-	-	-	0.5	
Iron,	-	-	-	-	0.9	2.0
Sulphur,	-	-	-	-	0.6	
						100.00

14. Calcination of Coarse-metal.—The fusion in the “ore furnace” having separated much of the gangue, silicious and earthy constituents of the ore, the metalliferous portions are now more readily acted upon, under the oxidizing influence of this calcination. The calcination of coarse-metal is effected in charges of about $3\frac{1}{2}$ tons of the dried, granulated, or crushed coarse-metal, which is placed upon the flat bed of a furnace similar to the “calciner” already described; the object of the operation being the oxidation of the iron in the coarse-metal in order that it may then be removed in the slag at the next fusion. The oxidation is attended at the same time with the elimination of a further portion of the sulphur as sulphurous anhydride and sulphuric acid; but the calcination is not pushed sufficiently far to effect the removal of the whole of the sulphur, a certain amount of the latter being required to combine with the copper for the production of a matt of cuprous sulphide or “fine metal” in the subsequent fusion. This calcination is also attended with the

elimination of a portion of the arsenic and antimony which passes into the matt of coarse-metal in the fusion in the ore furnace. The heat during calcination is maintained very moderate for the first 6 hours, after which it is gradually raised until the completion of the process, which occupies altogether from 24 to 36 hours; but it is at no point allowed to rise sufficiently high as to fuse the metal; while to prevent clotting, and at the same time to expose the metal more thoroughly to the oxidizing influence of the atmosphere, the charge is stirred or rabbled at frequent intervals. The "*calcined coarse-metal*" thus produced, is a blackish friable mass, containing sulphides of copper and iron, along with oxide of iron; the sulphur being present to the extent of about one-half the amount in the coarse-metal *before* calcination.

15. Melting of the Calcined Coarse-metal.—In this operation, the calcined metal from the previous calcination is melted along with products containing oxide of copper, such as *roaster* and *refinery slags* from the fifth and sixth operations; and an addition of ores of copper, consisting of oxides or carbonates, such as Australian ores, is also made when such are available; copper scale from the rolling mill, and broken hearths are also occasionally added. The furnace employed is similar to the ore furnace, figs. 4 and 5, with the exception that the hearth is without a basin, and slopes from all parts to the tap-hole. The process is conducted much in the same manner as the first fusion, except that the temperature employed is somewhat higher in this melting, and the operation is about 2 hours longer in duration. The charge, consisting of about 1 ton of calcined coarse-metal, with 12 cwt. of the slags and ores already mentioned, is spread over the furnace bottom, when the doors are well closed, and after about an hour fusion commences, and in from 3 to 4 hours the charge is well stirred, and the heat raised so as to thoroughly melt the charge. When charges of 50 cwt. are employed, the mixture is frequently made up of about 30 cwt. of calcined coarse-metal, 15 cwt. of oxidized ores of copper, and about 5 cwt. of roaster and refinery slags.

During the melting very little sulphurous anhydride (SO_2) is evolved, the reactions involved consisting mainly of a double

decomposition between the ferrous sulphide and the oxidized compounds of copper, whereby oxide of iron and cuprous sulphide result, of which the former, combining with silica derived from the slags and ores added to the charge, as also from the materials of the furnace, passes out in the slag as a fusible silicate of iron, which is skimmed from the surface of the regulus, and drawn out at the end door into sand moulds; while the latter or cuprous sulphide constitutes the regulus or matt of "*fine metal*," which is tapped out into sand moulds. The first pigs are the least pure, and if it be intended to produce *best-selected* copper, then the last pigs that are cast, along with the upper portions of the pigs first run out, are separated and used for that purpose, while the *bottoms* of the latter, being more impure, are then treated separately for the production of *tile copper*.

The regulus produced in this fusion varies in composition according to the amount of oxidized products at command for addition to the melting charge. If oxides or carbonates of copper are added in sufficient quantity to decompose the whole of the ferrous sulphide in the calcined coarse-metal, then the regulus is of a dark bluish-grey colour, with a semi-metallic lustre, brittle, and very compact, constituting what is known as "*white metal*," which has nearly the composition of cuprous sulphide (Cu_2S); but if the proportion of oxidized compounds of copper be insufficient to decompose the whole of the ferrous sulphide, then a larger amount of the latter occurs in the regulus, rendering it bluer in colour than the previous named, when it is then known as "*blue metal*"; while a third variety of the regulus known as "*pimple metal*" (from the pimple like excrescences occurring on its upper surface), occurs when the oxidized portions of the charge are in excess, which, with the exception of its pimpled surface, is much the same in physical qualities and composition as white metal, though occasionally it is somewhat redder in colour from the presence of metallic copper and cuprous oxide. *Blue metal* and *pimple metal* always contain metallic copper diffused through the mass; in blue metal the copper occurring as fine filaments in the interior of cavities, also as fine strings and angular particles throughout the mass of the regulus.

The slag of this melting, known as "metal slag," is of a dark, bluish-grey colour, sometimes iridescent and semi-metallic in lustre; it is brittle, compact except towards its upper surface, where cavities occur as though caused by enveloped bubbles of gas; and it may be granular, crystalline, or conchoidal in fracture, and from the sharp edges of the fractured fragments it is sometimes called *sharp slag*. In composition, *metal slag* is essentially a ferrous silicate with small quantities of other metallic oxides; and certain proportions of this slag are usually added to the charge in the fusion for "coarse-metal."

The following analysis of white metal, blue metal, and metal slag, are by Le Play:—

	White Metal.	Blue Metal.
Copper,	77·4	56·7
Iron,	0·7	16·3
Nickel, cobalt, and manganese,	Traces.	1·6
Tin and Arsenic,	0·1	1·2
Sulphur,	21·0	23·0
Slag and sand mechanically mixed,	0·3	0·5
	99·5	90·3

COMPOSITION OF METAL SLAG.

Silica,	-	-	-	-	-	
Alumina,	-	-	-	-	-	1·5
Ferrous Oxide,	-	-	-	-	-	56·0
Cuprous Oxide,	-	-	-	-	-	0·9
Various other Oxides,	-	-	-	-	-	2·1
Lime,	-	-	-	-	-	1·4
Magnesia,	-	-	-	-	-	0·3
Slag mechanically mixed	{	Copper,	-	-	-	2·9
		Iron,	-	-	-	0·3
		Sulphur,	-	-	-	0·8

100·0

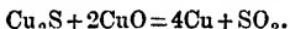
The invariable presence of metallic copper in blue metal, which occurs only exceptionally in white metal, together with the non-formation of a stratum of metallic copper in the furnace, which must occur if metallic copper existed in

the free state in the furnace, has led to numerous hypotheses as to the causes of its occurrence in blue metal. Le Play suggested that it was produced by the reaction of the slag and metal after pouring; but since the copper is distributed throughout the mass, and not merely along the line of junction of the metal and slag, this theory appears untenable. Dr. Percy concludes that the metallic copper exists in the metal of the furnace, dissolved in the bath of cuprous and ferrous sulphides, or blue metal, like graphite in pig-iron, and that it separates throughout the mass during cooling and solidification, again entering into a state of solution when the blue metal is remelted, in a manner analogous to the behaviour of graphite in pig-iron under similar circumstances. This explanation would indicate that the proportions of ferrous and cuprous sulphides, as existing in blue metal, possessed this solvent action upon metallic copper, which cuprous sulphide with a smaller proportion of ferrous sulphide, as existing in "white metal," did not possess.

16. Roasting for Blister Copper.—The operations up to this stage have resulted in eliminating from the copper ores the greater portion of their arsenic and iron, and a large proportion of their sulphur, with the production of a *matt* or *regulus* of cuprous sulphide, containing also ferrous sulphide and smaller quantities of other metals; a certain proportion of *sulphur* having been *purposely retained* in the product as the medium for concentrating the copper, while silica has had the effect of gradually withdrawing the iron originally present in the ore mixture. But the object of the present operation, known as "roasting," is to effect the removal of the remainder of the sulphur in the form of sulphurous anhydride; and of arsenic, antimony, iron, cobalt, nickel, tin, etc., either as volatile oxides, or as silicates passing out in the slag, with the separation of a more or less pure metal known as "blister copper." The active agents in this operation are the *oxygen* of the air and *silica*, a quantity of the latter always adhering as sand to the pigs of fine or blue metal, and a small quantity of quartz is also occasionally added along with the pigs of fine metal constituting the charges.

From 3 to $3\frac{1}{2}$ tons of the regulus or metal from the last operation are placed on the bed of a reverberatory fur-

nace, similar to that used in the last process, except that it is not provided with a hopper, the pigs of metal being introduced through a side door on to the hearth; and the air is also admitted to the hearth during the roasting, through two openings in the brickwork across the angles at the corners of the bed nearest the fire-grate end, or through the fire-bridge, according to Sheffield's plan of construction described in pages 27, 28. After the insertion of the charge the doors are closed, when the heat is raised and the metal gradually melts and runs down into the hearth, thereby exposing, during the melting-down stage, a large surface to the oxidizing action of the air, whereby a proportion of the sulphur is eliminated as sulphurous anhydride by the direct action of atmospheric oxygen upon the cuprous sulphide, and at the same time a proportion of the copper is oxidized, when the oxide so formed reacts upon the sulphide in contact with it, yielding sulphurous anhydride and metallic copper; thus,



In about five hours the charge is perfectly fused, when its surface presents the appearance of ebullition, due to the escape of sulphurous anhydride as the result of a violent reaction between the sulphide and oxide of copper, according to the above equation. The slag is now raked out from the surface, and the temperature is allowed to fall slightly by opening the furnace door, when the regulus becomes viscous, and its surface "rises" from the efforts of the gas within the mass to escape through the hardened crust of the surface, thereby increasing the surface of metal exposed to oxidation. After ten or twelve hours, sulphurous anhydride ceases to be evolved, when the heat is again raised, and a further escape of sulphurous anhydride takes place, by the mutual decomposition of the oxide and sulphide of copper contained in the metallic bath, during which stage the bath is rabbled so as to more thoroughly incorporate these substances, and in the last stage, when the furnace door is closed and the heat is at its greatest intensity, the metallic oxides—chiefly iron with any oxide of copper remaining undecomposed—unite with the silica, with the production of a fusible silicate or slag, known as "*roaster slag*," which is skimmed off and the metal (blister

copper), is tapped into sand moulds. The process thus occupies about twenty-four hours for its completion, and the product known as *blister copper*, from its blistered surface and vesicular character, is brittle, of a dull red colour, and contains about 95 per cent. of metallic copper, the residue consisting of traces of sulphur, arsenic, iron, tin, etc. The *roaster slag* is a scoriaceous, dark reddish-brown mass, often rich in oxide of copper, with shots of metallic copper distributed throughout its mass, and containing occasionally as much as 47 per cent. of silica, derived as already noted from the sand adhering to the pigs of fine metal, from the sides and bottom of the furnace, and from the quartz sometimes added to the charge. Roaster slag is one of the ingredients of the charge in the fourth operation or fusion for fine metal.

The following analyses of roaster slag and blister copper are by Le Play—

Roaster Slag.		Blister Copper.	
Silica, -	47·5	Copper, -	98·4
Alumina, -	3·0	Iron, -	0·7
Cuprous Oxide, -	16·9	Nickel, Cobalt, and	
Ferroous Oxide, -	28·0	Manganese, -	0·3
Oxides of Nickel, Cobalt, and		Tin and Arsenic, -	0·4
Manganese, -	0·9	Sulphur, -	0·2
Stannous Oxide, -	0·3		
Lime and Magnesia, -	Traces		
Metallic Copper, -	2·0		
	98·6		100·0

17. Refining or Toughening.—This, which forms the concluding operation in the Welsh method of copper smelting, is for the production of commercial copper, known as *tough-cake* copper, from the blister copper of the last operation; and for which purpose from 6 to 8 tons of the pigs of blister copper are introduced into a reverberatory furnace, with a larger proportion of grate area than in the melting furnace (figs. 4, 5) already described. The furnace is also without hopper in the roof, or hole through the bed, and has no side tap-hole, while the bed inclines from all parts towards the dished or hollowed portion in which the metal collects near the door at

the end of the furnace nearest the stack. The cakes of blister copper are arranged on the furnace hearth in the form of a hollow pile, reaching almost to the roof of the furnace, and thus allowing a free circulation of the air amongst them during the period of melting down. After introducing the charge the heat is gradually raised, but not too rapidly, the object being to oxidize or calcine the metal during this earlier stage, and in about 5 hours the metal is beginning to melt, and the heat is continued for 12 or 13 hours longer, constituting the first stage of this operation, during which time the more oxidizable metals, arsenic, iron, tin, antimony, zinc, and lead, with sulphur and some copper, will have been converted largely into oxides; the arsenic and sulphur being converted into arsenious and sulphurous anhydrides respectively, and which are volatilised. In order to separate the remaining oxides, the temperature is raised still higher, and continued for from 3 to 4 hours, when the surface of the metallic bath becomes covered with a hard scoria or slag, externally dark or almost black in colour, but of a reddish-brown colour on fracture; this slag is raked off through the end opening of the furnace, and the melted metal is then ready for the second stage, viz., *poling* or *refining* proper. The surface of the metallic bath is now covered over with powdered anthracite or ground charcoal to prevent its further oxidation, and a pole of green wood, usually birch, is thrust beneath the surface of the metal, when the gases and vapours disengaged by the decomposition of the wood thoroughly agitate the fluid metal, and every portion of it is brought into contact with the reducing gases, whereby any oxide of copper is reduced to the metallic state. The *poling*, as this operation is called, is continued for from 15 to 30 minutes, during which time samples of the metal are taken out at intervals and tested for malleability and ductility, by hammering into a plate and bending in a vice; and when the tests thus applied indicate that the metal has acquired the necessary toughness; and the fracture shows that the brick-red colour, with dull granular appearance of *under-poled* or *dry copper*, has given place to a salmon-red colour and a silky lustre, then the poles are withdrawn, the anthracite pushed back, and casting of the metal commences;

in which operation the copper is ladled from the furnace in ladles lined with fire-clay, and cast in various shaped moulds of iron or copper, the metal so cast constituting "tough-pitch" or "tough-cake" copper, or if, instead of casting in moulds, the metal be granulated by pouring it into cold or hot water, it is known as *bean-shot* and *feathered-shot* respectively.

The metal before *poling* commences is in the condition known as "dry copper," that is, it contains a considerable amount of cuprous oxide (Cu_2O) dissolved in the bath of metallic copper, and if examined in the cold state it is of a deep-red colour with a tinge of violet, yielding a coarse granular fracture, while it is quite brittle and void of the toughness characteristic of the final product. If the poling be continued too long, even by only a few minutes, the silky appearance and bright lustre of the copper gradually disappears, the colour becoming decidedly more orange, and the fracture also more coarsely granular: at the same time the metal loses its malleability and ductility, becoming even more brittle than dry copper; the metal in this condition is known as "*overpoled*" copper, to rectify which effect when produced, the surface of the fluid metal is exposed, after raking off the scoria, charcoal, etc., from its surface, to the oxidizing influence of the air from the doors and the fire of the furnace, by which exposure its toughness is again restored; and if during the lading the metal should become more or less *dry* from the oxidation going on at its surface, the poling is often resumed for a short time.

Pigs of copper in the *underpoled* or *dry* state always show a decided furrow along their upper surface, while in the *overpoled* condition the metal rises in the mould; or if a narrow ingot, then the furrow will be replaced by a decided ridge running along the length of the ingot, the depth of furrow or elevation of the ridge affording an indication of the degree of underpoling or overpoling of the metal; while in "tough-pitch" copper the upper surface of the pigs are flat, with the exception of small transverse furrows and ridges.

The brittleness of *underpoled* or *dry copper* may be due, in the absence of foreign metals, to the presence of an undue amount of cuprous oxide (Cu_2O) in the metal, since pure

copper is capable of taking up, when in the fluid state, a certain proportion of cuprous oxide which it retains on cooling, and copper so holding the oxide in solution is notably dry. But in the case of *overpoled* copper two explanations have been offered to account for its brittleness, the older one considered it to be due to a combination of carbon (from the wood used in poling) with the metal after the whole of the cuprous oxide present in the dry copper had been removed; but the more modern and generally accepted explanation is, that since all commercial copper contains more or less impurity, notably sulphur, tin, lead, and antimony, which render the metal brittle and red-short, an effect which is counteracted by the presence of a small proportion of cuprous oxide in the metal (see page 15); and that in *overpoled* copper, the whole of the cuprous oxide (Cu_2O) is reduced to the metallic state, by the carbonaceous matters and reducing gases produced in the poling operation, and brittleness of the metal accordingly results; but that, by exposing the surface of the melted metal to the action of the atmosphere for a short time, an amount of cuprous oxide may be introduced sufficient to neutralise the deleterious effects of the foreign metals, while the amount of oxide necessary to thus introduce will depend upon the proportion of foreign metals present in the copper.

If the blister copper contain large proportions of iron, arsenic, tin, etc., the refining is facilitated by the addition of a little lead, which is well rabbled with the charge, when the scum rising to the surface will contain the oxides of those metals along with oxide of lead, etc.; but after adding lead it is necessary to continue the rabbelling so as to effect the removal of the whole of the lead (as litharge) from the copper prior to casting.

If the copper be intended for rolling, from 2 to 15 lbs. of lead per ton of copper is added to the metal.

The slag produced in the refining or toughening, and known as "refinery slag," is rich in cuprous oxide, and usually contains shots of metallic copper distributed throughout its mass. It forms a portion of the charge introduced in the fourth operation or fusion for fine metal. The following analysis of refinery slag is by Le Play.

REFINERY SLAG.

Silica,	-	-	-	-	47.4
Alumina,	-	-	-	-	2.0
Cuprous Oxide (Cu_2O),	-	-	-	-	36.2
Ferrous Oxide,	-	-	-	-	3.1
Oxide of Nickel, Manganese, etc.,	-	-	-	-	0.4
Stannous Oxide,	-	-	-	-	0.2
Lime,	-	-	-	-	1.0
Magnesia,	-	-	-	-	0.2
Shots of Metallic Copper,	-	-	-	-	9.0
					—
					99.5

In addition to the six processes tabulated and just described for the production of tough-pitch copper, it is the general practice in the copper works to introduce, between the fourth and sixth stages previously described, two or more supplementary operations, consisting of an alternate roasting and fusion, which are conducted in furnaces similar to those already indicated, and the operations are carried on after the manner of the calcinations and fusions already described. The subjects of operation in these processes are fresh ores of the richer and purer classes along with the slags, etc., containing copper, produced in the fourth and subsequent operations of the previous smeltings; the regulus thus obtained being added to the general yield of fine metal from the fourth operation, and passes along with it as the charge of the fifth or *roasting* stage already described. Also, if only an insufficient supply of oxidized copper ores be at command for addition to the charges of the various operations, then the calcinations and fusions require to be repeated a greater number of times. Under these circumstances the regulus or blue-metal produced in the fourth fusion or melting of the calcined coarse-metal is not at once subjected to the *roasting* process, but is again calcined and subsequently melted before roasting, whereby the smelting will involve at least eight operations instead of the minimum number of six operations indicated in the previous pages.

18. Best-selected Copper.—The copper employed in the manufacture of the best kinds of brass, gun-metal, coinage, and other alloys is of the purest variety of commercial copper known as "best-selected," so called since for its preparation

the pigs of fine metal or other regulus of a similar composition undergo a process of selection; whereby the pigs that are first tapped out in the melting of the regulus, and which contain the greater portion of the tin, antimony, arsenic, lead, nickel, etc., and other impurities of the ore, are separated, and treated apart from the pigs cast towards the conclusion of the tapping. The former, after roasting and refining in the usual manner, yield an impure metal known as "bottoms" or "tile-copper;" while the latter yield, after the same treatment, an almost pure metal known as *best-selected* copper. Also since the alloy of copper with tin and the other foreign metals is more dense than the pure metal, the alloy settles to the bottom of the pigs during their solidification, and is detached by the hammer from the upper portions immediately the metal sets, when the upper portions are treated for best-selected, while the lower yield only an inferior metal known as *bottoms*.

The melting and casting is usually repeated a second time upon the selected portions of the first cast, and the same selection made of the purer portions. In this manner about one-fourth of the copper is rejected in the selecting process at each melting, so that in the two meltings about one-half of the original charge of white metal is treated for best-selected, and the other half forms bottoms or tile-copper.

Another method consists in *roasting* the regulus of *blue*, *fine*, or *pimple* metal, until about one-half of it has melted or liquated out, when the melted portion forms the most impure metal; since the melted copper in passing through the stanniferous compounds contained in the regulus decomposes them, and the reduced tin, etc., alloying with the copper, and liquating or sweating out, is drawn off; while the residue known as *regule*, *best regule* or *spongy regule* is treated separately for *best-selected*; and if necessary the regule first obtained is subjected to a second or a third partial roasting, when the regule so obtained is usually free from tin, arsenic, etc. As in the previous method the regulus separated during these partial roastings produces an impure metal known as *bottoms*. Best-selected copper should also be prepared exclusively from the purest copper ores.

The *bottoms* produced in these processes are very impure

and of variable composition, containing from 75 per cent. to 90 per cent. of metallic copper, the remainder consisting of tin, antimony, lead, iron, nickel, manganese, arsenic, and sulphur, in very variable proportions.

19. Elimination of Foreign Metals, etc., in Copper Smelting.—As noted above, the *selecting* process effects the elimination of many foreign metals from the copper; in this manner *gold* and *silver* are largely if not wholly obtained in the bottoms produced in the process, while the copper smelted from ores containing these metals, if not subjected to the selecting process, will contain gold and silver diffused throughout the metal. *Antimony*, also, which occurs in the grey antimonial copper ores and in some of the Australian ores, is eliminated in the selecting process passing out in the bottoms, but possibly a portion may likewise be volatilised as antimonious oxide (Sb_2O_3) during the calcinations of the ore, etc.

Tin, again, is separated in the bottoms during the selecting process, and occasionally the amount of tin so separated is sufficiently large to give a white appearance to the metal forming the bottoms, which is then known as *hard metal*. The tin is originally present in the ores probably as stannic oxide (SnO_2), which in contact with copper or iron pyrites would probably yield stannous sulphide in the first calcination of the ore, attended with the evolution of sulphurous anhydride; and, as detailed under the selecting process, metallic copper coming into contact with stannous sulphides during the partial roasting in the best-selecting process, effects a reduction of the tin, with the production of a regulus of cuprous sulphide, accompanied by an alloy of tin and copper, which latter being more dense than the copper sinks and forms the lowest stratum or *bottoms*. Crystals of stannic oxide are occasionally found also in the slags produced in copper smelting, as also in the stacks of the roasting furnaces.

Arsenic is usually present in the smelting mixture of copper ores, as mispickel, arsenical iron, grey copper ore, etc., and is partially evolved as arsenious anhydride (As_2O_3) in the various roastings, and at the same time a portion is retained as basic arseniates of iron and copper, which latter compounds, when heated to a high temperature in contact with silica, as in the several fusions of copper smelting, are resolved into arsenious

anhydride, oxygen, and silicates of iron and copper. A further portion of the arsenic is possibly eliminated as arsenious fluoride (which in contact with moisture is resolved into arsenious anhydride and hydro-fluoric acid), by the action of hydro-fluoric acid and silicic-fluoride upon the ore, since hydrofluoric acid (HF) would be produced by the reaction of the sulphuric acid, generated by the oxidation of sulphur in the roasting process, upon fluor spar (CaF_2) sometimes present in the ore mixture, while the silicic-fluoride (SiF_4) would result from the action of hydro-fluoric acid upon the quartz always more or less present. Arsenic is also separated in the selecting process, passing out with the other impurities in the bottoms.

Nickel and *cobalt* occur occasionally in considerable quantities in copper ores, and unless a special operation be conducted for their concentration, these metals will occur partly in the refined copper, and partly in the slags and bottoms. Mr. Vivian patented a method for the separation of nickel and cobalt from ores, slags, or regulus of copper, in which he converts these metals into *arsenides* or *spcise*, while the copper is separated as *sulphide*. For this purpose, if the nickel, cobalt, and copper exist in an *oxidized* state, as in slags or oxidized ores, the material is then mixed with arsenical pyrites, and sufficient sulphur, in the form of iron pyrites, as is required to combine with the copper, along with coal or carbonaceous matters, to effect the reduction of the oxides. The mixture is then melted and tapped out, when the arsenical compound sinks to the bottom of the pigs and is detached from the upper portion or regulus of copper, the melting being sometimes repeated a second or third time for the better separation of the two products. The bottoms so obtained contain from 1 to 12 per cent. of nickel and cobalt, with from 15 to 50 per cent. of copper, together with some antimony, iron, etc. If the nickel and cobalt do not exist in the *oxidized* state, and are not present in large quantities, then they are separated from the copper after the latter has attained to the condition of white metal; the white metal being roasted as in the selecting process, and an addition of about one-eighth of its weight of arsenical pyrites is made at the completion of the first stage of the roasting, *i.e.*, just before melting down, when, on tapping, the *speise* will occur as bottoms in the four

or five pigs of metal nearest the tap-hole. By a second treatment of the concentrated nickeliferous product produced by either of these methods, Mr. Vivian proposed to obtain the *speise* in a marketable form.

20. Method of Copper Smelting Patented by Napier.—Numerous patents have been taken out for reducing the number of operations involved in the smelting of Cornish or similar ores, and for the better separation of the tin, antimony, and arsenic from the product. Of this class is that of Mr. Napier, which involves four operations preparatory to the refining of the copper, instead of the minimum of five, required in the ordinary method. In the first operation of Mr. Napier's process, the mixed ores are calcined during nine hours, which operation is succeeded by a fusion, as for coarse-metal in the Swansea method, and for this purpose the calcined ore is withdrawn from the calciner and mixed with a quantity of cobre or other rich ore, in proportions judged to be necessary for the production of a fusible slag of ferrous silicate, and a matt containing from 30 to 50 per cent. of copper, the fusion being effected in a reverberatory furnace; and, before tapping, the scoria and slag are skimmed from the surface, when 120 lbs. of salt cake (crude sodic sulphate), with 40 lbs. of slaked lime and 60 lbs. of coal are added for each ton of metal in the charge. The mixture is then well rabbled, and after a quarter of an hour the metal is tapped into sand moulds, from which, as soon as the metal is solidified, it is removed and thrown into tanks of water, where the pigs rapidly disintegrate and fall to powder. In the fusion the salt cake is reduced to the condition of sodic sulphide by the coal introduced with the charge, and this sulphide combines with the sulphides of antimony, arsenic, and tin present in the regulus, the whole of which are then dissolved out in the lixiviation. In the third operation, the finely divided and dried residue from the lixiviation, obtained after syphoning off the liquid, is calcined in large calciners, having three beds in vertical height, one above the other, over which the products of combustion from the furnace pass in succession, the material being first introduced on to the upper bed, then raked on to the middle, and lastly on to the lower bed of the calciner; in this manner about 12 tons

of regulus is roasted almost perfectly sweet in from twenty-four to thirty hours. The copper exists in this calcined product largely as oxide, for the reduction of which it is mixed with fine anthracite, and at the same time a quantity of ore, free from sulphur and arsenic but rich in silica, is added, whereby on fusing in a melting furnace, which constitutes the fourth operation, the iron is separated as a fusible slag or silicate, beneath which is the reduced metal ready for the refining process. Mr. Napier's method has however been replaced at the Spitty works, near Swansea, where it was applied, by the old method of copper smelting.

21. Method of Rivot and Phillips.—In the method of copper smelting proposed by these gentlemen, the ore is reduced to powder and roasted sweet, when the roasted ore is melted in a reverberatory furnace along with lime, sand, or slags; and bars of iron are then introduced through apertures made for the purpose, into the bath of silicates on the hearth, whereby the more oxidizable metal, iron, replaces the copper in the silicate, while the liberated copper subsides to the bottom of the bath. The copper produced is, however, likely to be ferriferous, unless great care be exercised to support the bars of iron in the slag out of contact with the precipitated copper; and also if the ores contain tin, antimony, or arsenic, these bodies are likely to occur more or less along with the copper to the deterioration of its quality; while the process is further attended with the consumption of iron, about equal in amount to that of the copper produced.

COPPER SMELTING IN BLAST FURNACES.

The method of smelting in *reverberatory* furnaces as practised in England, is alike suitable to almost all classes of ores, but it entails a very large consumption of fuel, and is therefore often replaced, where fuel is scarce and dear, or where the ores are of a more simple and purer character than those employed in England, by the method of smelting in *blast* furnaces; as also if either very rich or very poor ores be worked alone, the method of reduction in the blast furnace appears preferable. Accordingly, we find the blast furnace in use for copper smelting in Sweden, Saxony, Hungary, Russia, etc.

22. Copper Smelting in Sweden.—At the works of

Atvidaberg, in Sweden, the ores are poor, yielding only from 4 to 5 per cent. of black copper, and are divided into two classes, viz., "hard" and "soft," according as quartz or other hard matters preponderate over the metallic sulphides, or otherwise. The *hard* ores contain copper pyrites, zinc blende, and a little iron pyrites, accompanied by much quartz, felspar, mica, calspar, etc.; while the *soft* ores contain a large proportion of zinc blende with magnetic pyrites and magnetic iron ore, with smaller proportions of quartz, silicious matters, etc. The smelting of these ores involves four operations, consisting of two calcinations or roastings and two fusions, exclusive of the refining of the black copper produced in the *blast furnaces* employed in the two fusions.

1°. The ores are *roasted* or *calcined* in pyramidal heaps or in kilns, the heaps are about 30 feet square, and 10 or 12 feet in height, formed by first laying a bed of wood upon the surface of the level ground, upon which is placed alternate layers of ore (broken into pieces of the size of an egg) and small charcoal, the surface being covered over with small ore, and ore dust. The wood in the bottom is then ignited, after which the heat is maintained from four to six weeks, by the combustion of the charcoal and sulphur of the ore; with *soft* ores the roasting is required to be repeated for a second time, lasting from three to four weeks, for which purpose the ore is again broken up, since portions of it, due to irregularity in the temperature, will have sintered together, while other portions will be perfectly roasted. The kilns sometimes employed, instead of the heaps, are bins or stalls formed by three walls, a back and two sides, while the top and front are open, and two of these are generally built together in the same line. The kiln is charged in the same manner as the pyramidal heap, with alternate layers of fuel and ore, with a continuation of the combustion for a like period as in the heaps. When the ore contains much zinc blende, the first stage of the calcination is marked by the emission of much smoke, and the surface becomes coated with zincic oxide.

2°. This stage consists in the production of a regulus containing from 20 to 30 per cent. of copper, obtained by treating the roasted ore along with *black copper slags* from the

fourth operation, and, occasionally, also carbonate of lime, in a *blast furnace*, figs. 6, 7, known as the *ore furnace*, which is provided with four, or, in the more recently constructed furnaces, with three horizontal twyers *a*, *a*, *a*, placed in the arch *f*, of the back wall of the furnace. The shaft of the furnace is rectangular in section, the back wall being vertical, while the front wall, supported upon the tympanum iron *b* and an iron girder, rises vertically for a short distance, then inclines towards the back, and so narrows the section of the stack towards the top; the *hearth* projects beyond the line of the front wall, and the *tap-hole* is situate at one corner of the fore-hearth so formed. The hearth is lined with a mixture of clay and sand well rammed in, and beneath is a drain for the escape of moisture. These furnaces measure from 20 to 24 feet in height, and are about 4 feet in diameter at the level of the twyers.

Smelting in these furnaces is most frequently attended with the production of a ferriferous mass or "bear," which collects in the bottom of the hearth; and resulting from the presence of incandescent carbon, together with the reducing atmosphere of carbonic oxide in the furnace, whereby a proportion of the oxide of iron, formed in the roasting of the iron pyrites contained in the ores, is reduced to the metallic state according to the reactions described under iron smelting; and these masses accumulate the more rapidly if the roasting be carried too far, and less slowly if a proportion of sulphur be left in the ore. Indications of the working of the furnace are afforded by the appearance of the *furnace eye*, at the end of the slag prolongation of the twyer, under which the furnace

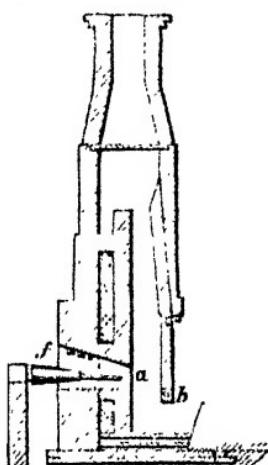


Fig. 6.—SWEDISH BLAST FURNACE FOR SMELTING COPPER.

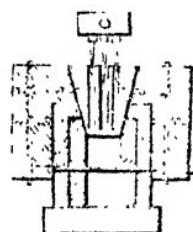


Fig. 7.—PLAN OF SWEDISH FURNACE.

is always worked; for if too much slag be added to the charge, the nose forms too rapidly, whilst the reverse is the case if an excess of fuel be added. The furnace being at work, the *regulus* and *slag* collect in the hearth, and at intervals about two-thirds of the slag, which is essentially a ferrous silicate floating above the regulus, and will not contain more than .25 to .5 per cent. of copper, is tapped out into sand beds and thrown away, while the remainder is returned to the ore furnace with succeeding charges. The furnace is only finally tapped when the hearth has become quite filled with regulus, which usually happens in from two to three days, when it will contain about 5 tons of metal, which is run out into sand beds, and when cold it is broken into pieces for roasting in the next (third) operation. The fuel employed is either coke or charcoal, latterly the former has come into more general use, and the practice of using hot instead of cold blast has been introduced. Oxide of zinc present in the roasted ore is reduced in the furnace and the metal volatilised, but again becomes oxidized as it passes through the stack of the furnace, where it forms a white coating around the throat which requires to be detached at intervals.

3°. Is a series of *roastings of the ore furnace regulus*, conducted in kilns formed by a central wall, to which are built partition walls at right-angles, so forming a number of rectangular bins, back to back, each capable of holding about 5 tons of the regulus or matt. The kiln is made up by spreading a depth of 6 or 8 inches of wood over the bottom, upon which is piled the lumps of regulus. When the firing is completed the ore is turned over, broken up, and transferred to the next bin, and so on for five or six firings, each alike, except that in the first firing no fuel beyond the first layer is added, whilst in each succeeding charge an amount of charcoal, increasing in weight with each firing, is placed in the kilns with the regulus; the roasting, consisting thus of a series of firings, is completed in from seven to eight weeks.

4°. *Fusion for black copper* is conducted in blast furnaces of the form represented in figs. 8 and 9.* They are about 17 feet in height, and 3 feet in diameter at the twyers; and a portion of the gases are taken off from these furnaces about

* *Bredberg Bergwerksfreund.*

8 feet above the hearth. Such a furnace being charged* with 200 lbs. of the regulus from the last operation, 40 lbs. of roasted thin regulus (a regulus produced in a previous smelting for black copper), 20 lbs. of ore furnace slags, 20 lbs. of cupriferous products, and from 10 to 20 lbs. of quartz, according to the amount of silica already present in the mixture. The furnace is worked with a twyer prolongation or nose, of from 4 to 6 inches in length, and the breast of the furnace is closed with sand, except a small opening through which the flame blows during the working of the furnace. The products of the operation are *black copper*, so called from its black oxidized surface,

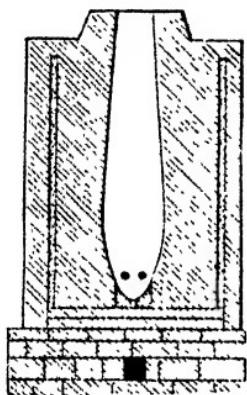


Fig. 8.—VERTICAL SECTION IN
FRONT OF THE TWYERS.

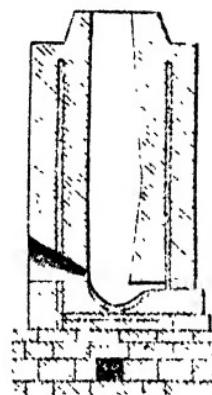


Fig. 9.—VERTICAL SECTION
THROUGH THE TWYERS.

which corresponds in composition very closely to the "blister copper" produced in the Welsh method of smelting; this is accompanied by a superstratum of *thin regulus* or *matt*, varying according to the proportion of copper from reddish-blue to steel-grey in colour, and containing from 55 to 72 per cent. of copper; this regulus, after roasting, being added to the charge of the same furnace in subsequent fusions; and forming the upper stratum is *black copper slag*, a portion of which is also returned to the furnace with future charges; while, lastly, there collects in the hearth of the furnace *ferriferous masses* or *bears*, like those described as occurring in the ore

furnace. It is for utilising the waste heat of the furnace, and at the same time to prevent as much as possible the formation of these masses, that the gases are drawn off from the furnace as described. When the melted matters in the hearth of the furnace reach almost to the twyers, the slag is drawn off into sand moulds, by removing a portion of the breastwork of the furnace, after which the breast is made up again and more materials are added to the furnace, with tapping of the slag as before, until a sufficient quantity of black copper and regulus have collected in the hearth as to require tapping-out, which occurs every two or three days; upon which the slag and regulus are drawn off close to the surface of the black copper, and the metal is tapped into a long iron channel divided into a number of compartments, forming a series of moulds, in which the copper is cast. Any regulus which runs out with the slag will collect beneath the first few pigs, which are turned over as soon as solidified, and while still hot are broken, whereby the regulus is easily separated from the slag.

23. Refining of Black Copper.—The refining hearth is an almost semicircular cavity, from 2 to $2\frac{1}{2}$ feet in diameter, and from 15 to 18 inches deep, constructed in a platform of brick-work, and lined with a refractory material, as fire-clay and sand well beaten down, the blast being supplied at a pressure of from $1\frac{3}{4}$ to $2\frac{5}{8}$ lbs. through a copper twyer projecting over the hearth, and inclined at an angle of 45° downwards. In conducting the process the hearth is first filled level with charcoal or coal, and three pieces of black copper placed along the sides of the hearth, upon which about 15 cwt. of pigs of black copper are placed one upon another, keeping a short distance from the twyer. Ignited fuel is then placed in front of the twyer, when the whole is covered with charcoal or coal, and the blast is gradually let on, so that the metal is melted down slowly, exposing thus a large surface for oxidation by the blast. When melted down its surface is kept covered with charcoal, and the slag, which varies in colour according to the oxides that it contains, becoming red towards the close of the operation from the presence of oxide of copper, is skimmed off two or three times during the process of refining; and for this purpose the blast is turned off, the

charcoal is pushed back, and water projected on to the surface by which the slag is solidified, and may be removed as a cake. Quartz is occasionally added to the charge if the slag is too thick from a deficiency of silicious matters. The progress of the refining is judged by the workman from the thickness, colour, lustre, and malleability of the small cylinder of metal withdrawn upon the end of a pointed iron bar, inserted at intervals into the metallic bath, and when the copper has attained the required condition, it is ladled into ingot moulds.

In some works of the Continent the English *rerverberatory* furnace has been introduced for the refining of the copper. In other Continental works, where the black copper is less pure than the above and the refining hearth is still used, the metal is first refined, and then remelted to *toughen* the metal for rolling and hammering in a similar hearth, with a horizontal or only slightly inclined twyer, when instead of ladling the refined metal into moulds its surface is cleared of charcoal, etc.; the metal is then allowed to cool down somewhat, and when at the proper temperature, water is sprinkled over the surface, whereby a crust is formed which can be removed as a thin disc of a rich red colour, constituting "rosette copper;" this operation being repeated until nearly the whole contents of the hearth has been removed in this form. During the cooling down, preparatory to sprinkling water upon its surface, the phenomenon known as "copper rain" is observed, in which minute shots of copper are thrown up in considerable quantity from the surface of the metal, the occurrence or otherwise of the copper rain appearing to depend upon the proportion of cuprous oxide contained in the metal; for if void, or containing only small quantities of the oxide, the rain is very perceptible, while with larger quantities the surface of the metal sets without throwing up any rain.

The discs of rosette copper obtained in the above manner are then remelted for *toughening*, trial specimens being taken out as before to ascertain its degree of toughness; and when it has attained the proper condition, it is then ladled into ingot moulds.

The process of copper smelting adopted at Fahlun and other places of Sweden, Norway, etc., do not differ essentially.

from that described as carried on at Atvidaberg. At Fahlun the ores are somewhat poorer than those of Atvidaberg, and the soft ores only are roasted, the hard ores mixed with the roasted ores passing at once to the blast furnace.

24. Copper Smelting in Japan.—In the preparation of Japanese copper the ore is first roasted in kilns along with the required fuel, and the roasted ore is smelted with charcoal in small primitive furnaces, supplied with a blast from bellows worked by manual labour, the *regulus* or coarse-metal so obtained (if the ore be rich the coarse-metal is accompanied by a proportion of metallic copper, forming the lowermost stratum in the furnace) is again roasted and remelted, after which it passes to the foundry, where it is refined under a blast of atmospheric air, and the refined metal is then melted in crucibles and cast under warm water into small ingots of about 1 lb. in weight; and in this manner the ingots are obtained with a clear bright surface of a rich red colour.

25. Smelting of the Mansfeld Copper-schist.—The ore of this district (Prussian Saxony), is an argillaceous and argentiferous copper-schist, occurring between the lower Permian sandstone and the magnesian limestone of the Permian formation, and constitutes the Kupferschiefer of the Germans. It forms a bed 10 or 20 inches in thickness, lying on a sandstone which is also, to the depth of 2 or 3 inches, sufficiently cupriferous to be profitably smelted. The schist is largely impregnated with bitumen, and contains copper disseminated as copper pyrites, vitreous copper, purple copper ore, grey, black, and red copper ores, with native copper, and these are accompanied constantly or occasionally by a large number of other minerals, amongst which are iron pyrites, zinc blende, kupfernickel, smaltine and other cobalt ores, with occasionally galena, etc., besides calcareous, silicious, and argillaceous matters in large proportion. The schist is very poor in copper, but owing to its argentiferous character, it can be profitably smelted if it contain not more than from 2 to $2\frac{1}{2}$ lbs. of copper per centner of ore, or from 2 to 3 per cent. of copper, the product usually containing about 0·5 per cent. of silver. The smelting of this schist is carried on at Mansfeld, Eisleben, Friedeberg, Sangerhäuser, and other districts of Prussian Saxony.

The smelting of the schist involves some eight or nine distinct operations, both the blast and reverberatory furnace being employed in its reduction. The raw ore or schist is first hand-picked and then roasted during eight, ten, or twelve weeks in pyramidal heaps or in kilns, in the manner described when treating of the Swedish copper smelting, the bituminous matters often being sufficient to carry on the combustion after being once ignited, whilst the less bituminous ores are not roasted. In this operation the bitumen and water are largely expelled, and a portion of the arsenic, antimony, and sulphur in the schist are also oxidized and eliminated. The roasted ore is then mixed with from 5 to 8 per cent. of fluor spar, and a like proportion of cupriferous slags from the subsequent stages of previous smeltings, along with other furnace residue; this mixture being smelted in small blast furnaces, using coke as fuel. The furnace employed, until recently, was from 18 to 20 feet in height, and had two twyters placed on the same or opposite sides of the hearth, the latter being square in section; while from the top of the hearth to the mouth the furnace is cylindrical in section, the bottom of the hearth sloping forward. In front of it are two pits or receptacles, each communicating with the hearth by a separate opening in the front of the furnace, from each of which apertures the *regulus* or *slag* flows alternately into the basins; for as one receptacle fills, its tap-hole is stopped and the other opened, and so on, so that the flow of melted matter is continuous, while the supply of ore and fuel to maintain it is added continually at the mouth of the furnace.

Latterly, the blast furnace (figs. 10 and 11) has been introduced; it is 30 feet in height by 6 feet in diameter, and is provided at the top with an apparatus for collecting the waste gases. These furnaces are driven by *hot blast*, and afford a daily yield about four times as great as the former furnace. The regulus collects in the hearth of the furnace, and is tapped out for granulation therefrom, through the tap-hole *a*, along the trough *d*, into the water cistern *b*; while the slag is tapped from the aperture *c* at a somewhat higher level, at the opposite side of the furnace. The products of this smelting are *coarse-metal* or "*Rohstein*," con-

taining from 30 to 40 per cent. of copper, with from $\frac{1}{8}$ to $\frac{1}{4}$ per cent. of silver; and a slag which is moulded into bricks

whilst in its pasty state, and then used as a building material. The coarse metal or Rohstein is broken up and roasted once or twice in stalls or bins, for the separation of sulphur, etc., the combustion being commenced by a layer of brushwood placed in the bottom of the bin, after which it is continued by the oxidation of the sulphur in the ore, and will usually last for from ten to twelve days, when the fire will have burnt out.

The roasted regulus is smelted, with the addition of slags from the second operation, and of quartz in the form of sand; the fusion being effected in a reverberatory furnace, resembling the Welsh furnace employed at the corresponding stage, the slag being skimmed off from the surface of the melted metal through a side door, and the concentrated metal, regulus, or "*Spurstein*," as the product is called, is tapped out into water for granulation. The fuel employed in

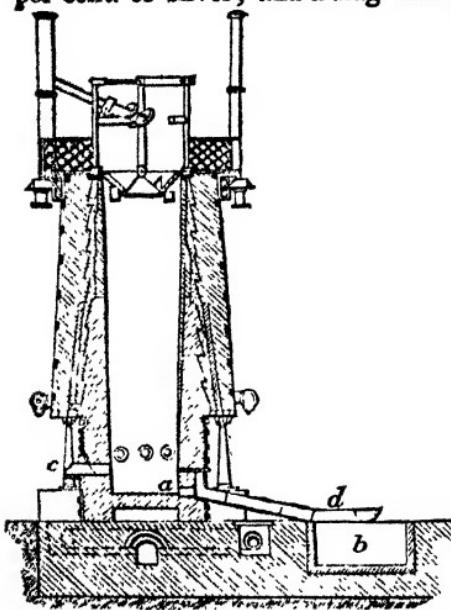


Fig. 10.—BLAST FURNACE FOR SMELTING THE MANSFELD SCHIST.

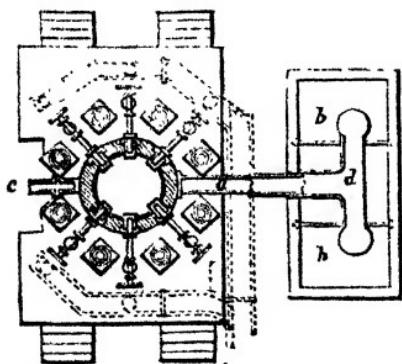


Fig. 11.—PLAN OF THE MANSFELD BLAST-FURNACE.

this fusion is a mixture of English coal, with a brown coal or lignite occurring in the neighbourhood.

The three ensuing operations of *grinding* and *roasting* of the concentrated regulus, and *lixiviation* of the roasted product, for the extraction of sulphate of silver, are (as will be subsequently described under the Zier vogel process for the extraction of silver) for the desilverization of the metal.

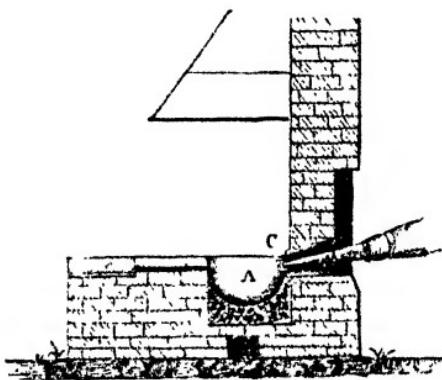


Fig. 12.—KUPFERGAARHED, OR REFINING HEARTH FOR BLACK COPPER.

The desilverised residue, containing about 70 per cent. of copper, chiefly as oxide, is mixed with 8 per cent. of clay, and sufficient water to allow of its being moulded by hand into balls of some 4 inches in diameter, which are then dried in hot chambers, and introduced along with stamped quartz or sand, ore-furnace slag, and either from 1 to 2 per cent. of the regulus from the previous conduct of this stage, or with iron pyrites free from silver, into a blast furnace along with alternate layers of coke, the furnace being driven by cold blast. The products of this operation in ascending order are *black* or "*blister copper*," forming two-thirds of the yield; then a layer of a "*thin regulus*" or "*matt*," between the blister copper and the slag, which regulus is returned for smelting in the same furnace, at a subsequent charge; while upon the top of the regulus is the "*slag*," forming about 30 per cent. of the yield, and which is broken up and sorted for the separation of any

regulus it may contain. The blister copper obtained in this smelting or fusion is *refined*, partly in reverberatory furnaces and partly in the German refining hearth (fig. 12), holding about 5 cwt. of metal, and in which the metal is refined under charcoal by a blast of air introduced through the twyer *d*, inclined at an angle of about 10° downwards; and when the metal has attained the proper condition, determined by trial pieces taken out on the end of a bar of iron, its surface is cleared of charcoal, etc., water sprinkled upon it, and the metal removed in cakes as "*rosette copper*," in the manner already described, which rosette copper, if required for hammering or *tough-pitch copper*, is toughened by melting down and poling in a reverberatory furnace after the method pursued in South Wales. The slags produced in the German refinery towards the end of the process are of a deep-red colour, and are extremely rich in cuprous oxide.

26. Copper Smelting in Russia.—The ore smelted at Perm, in Russia, is a cupriferous sandstone, yielding only from 2 to 3 per cent. of metallic copper, the metal in which exists chiefly in the oxidized state as blue carbonate of copper, malachite, chrysocolla (hydrated silicate of copper), oxides and vanadate of copper, with occasionally a little native copper, and rarely vitreous copper and copper or iron pyrites. This sandstone is smelted in cupola blast furnaces, resembling those described as in use at the Swedish works of Atvidaberg, but differ in having only one twyer, the smelting being effected with *charcoal* as the fuel, and about 30 per cent. of *dolomite* as a flux, rich refinery slags and slags from this same operation being also added to the charge. The compounds of copper, iron, etc., of the ore are thus heated in contact with charcoal, and in a reducing atmosphere of carbonic oxide, whereby both iron and copper are reduced; the iron, as explained under pig-iron, combining with a proportion of carbon, and in this case, at the same time, taking up a quantity of copper; and there thus occurs in the furnace hearth "*black copper*," "*cupriferous pig-iron*," and "*slag*." A furnace charged with the materials as above, smelts from $3\frac{1}{2}$ to $4\frac{1}{2}$ tons of ore per day of 24 hours; the metallic products (black copper and cupriferous pig-iron) being withdrawn from the furnace at intervals of 24 hours, while the slag

runs out from the fore-hearth as the metal collects. The cupriferous pig-iron, forming a stratum above the black copper, is removed in discs by sprinkling water upon its surface, whilst the black copper is either removed in the same manner, or is ladled out into ingot moulds.

The *cupriferous pig-iron* is a whitish, hard, granular body, containing from 3 to 12 per cent. of copper, partly in shots or grains disseminated throughout its mass, and for the separation of its copper, the discs are smelted with charcoal in a small hearth having a silicious lining, whereby black copper and a fusible slag of ferrous silicate results. Should this slag be *unclean*, i.e., still retain more than .5 per cent. of copper, it is melted in the blast or ore furnace along with other slags, when there results a highly cupriferous deposit or "*bear*," from which the copper is extracted as from the cupriferous pig-iron, by treatment on a small hearth; and accompanying the "*bear*" is a slag less basic than the former one.

The *black copper* is refined in a reverberatory furnace, having a slightly concave hearth formed of clay and coal-dust, and which slopes from the fire-bridge to the opposite end, where the slags flow out, and which end is also in communication with two circular cavities, into which the metal is withdrawn, and from whence it is either taken off in discs or ladled into moulds. One or two twyers placed at one side of the furnace, opposite the working door, direct a blast of air upon the surface of the melted metal, whereby the iron is oxidized and removed in the slag; for facilitating which, either silica (sand) is thrown upon the surface of the metal during the refining process, or, after the metal is melted, the blast is turned off and a quantity of pyritic ores (sulphides of copper and iron) along with silicious matters, are introduced and thoroughly melted with the charge; when a double decomposition ensues, whereby the oxide of copper in the slag and in the metal is converted into sulphide, which remains with the copper on the hearth, while the iron is oxidized and escapes in combination with silica as a flux or slag; and after the removal of the slags, the blast is again let on, and the refining continued for the removal of sulphur, etc., its progress being determined by samples taken out in the usual manner. From 2 to 3

tons of the black copper is refined at each charge of one of these furnaces.

REDUCTION OF COPPER BY "WET" PROCESSES.

The "wet methods" for the extraction of copper are only practicable in districts where fuel is dear, and the ores are very poor in copper, or in which the metal exists in a special state of chemical combination, such as very poor sulphides, oxides, or carbonates of copper, occurring in a silicious or other insoluble non-calcareous matrix or gangue; or where the metal exists as a salt of copper already dissolved in water, as in the waters flowing through certain copper mines, etc. The wet methods are also sometimes applied to richer ores if they contain silver, which can be extracted at the same operation; while in all cases the copper, precipitated or separated by a wet process, requires *fusing* and *refining* before it possesses sufficient malleability and ductility for application to most purposes for which copper is used. *Iron* is the usual precipitant employed in these processes, but calcic sulphides, ferric chloride, and sulphuretted hydrogen are also employed. The wet methods of extraction are pursued at Linz in Westphalia, at Rio Tinto, at Schemnitz, and other places on the Continent, and formerly also at Alderley Edge, Neath, etc., in England.

27. Bankart's and other Processes.—Bankart's process was for a short time carried on at Neath, in Glamorganshire, where the ore operated upon was the rich sulphide of copper imported from Cuba, such ores yielding about 16 per cent. of copper. These Cobre ores were ground to powder and roasted in charges of about 2 tons, during 24 hours, in a calcining furnace, constructed so that the products of combustion from the fire might pass along a flue beneath the bed, and not over the roasting ore, while air was admitted to the hearth through the bridge and at the sides of the furnace. During the roasting much sulphur is eliminated as sulphuric anhydride, whilst another portion is converted into sulphuric acid, which combines with the oxides of copper and iron formed during the calcination, with the production of cuprous and ferrous sulphates, and on carefully raising the temperature of calci-

nation, the ferrous sulphate, which is decomposed at a lower temperature than the cuprous salt, is converted first into the basic persulphate and eventually into ferric oxide, with the evolution of anhydrous sulphuric acid (SO_3), which serves to convert a further portion of the oxide of copper into cuprous sulphate. When the roasting is completed the charge is withdrawn from the furnace, and transferred to a series of dissolving vats having perforated false bottoms covered with canvas, the water for solution being introduced on to the top of the roasted ore in the first of the series, and is drawn successively from the first to the next below it, and so on to the last of the series; a jet of steam along with the water being likewise sometimes introduced for the better solution and extraction of the soluble salts of copper. In this manner cuprous sulphate and small quantities of ferrous sulphate are dissolved out, when the solution so obtained is transferred to the precipitating vats, *i.e.*, vats containing fragments or plates of *cast* and *wrought iron*. The solution passing from the highest to the next lower in the series, and remaining for a little longer time in each one of the series, from the first to the last, the solution depositing a proportion of its copper upon the surface of the iron plates in each vat; $\text{CuSO}_4 + \text{Fe} = \text{FeSO}_4 + \text{Cu}$, the copper so deposited requiring to be detached at intervals from the plates. The escaping water contains ferrous sulphate, and this is separated by crystallization, constituting a bye product of the process.

The residues from the lixiviation vats after drying are mixed with fresh ore, again roasted and passed through the same processes of lixiviation and precipitation for the more perfect extraction of the copper; this cycle of operations being repeated usually three times upon the same ore, with the addition of a quantity of a more highly pyritic ore at each roasting. The necessity of grinding the ore; the loss of copper from leakage, along with the loss in the residual ore, due to imperfect lixiviation, and to the presence of oxide of copper not converted into sulphate, or which after conversion has been again decomposed by the use of a too high temperature in the roasting operation, the amount thus left in the residue being in excess of that thrown away in the ore furnace slag; these, together with the great bulk of materials to be operated

upon, and the inability of the process to utilise the slag produced in the subsequent refining of the metal, have led to a discontinuance of the process.

In other processes for the conversion of *cuprous sulphide* into *sulphate* by oxidation, the roasting is conducted in mounds, or heaps, or in kilns, as in "*kernel roasting*," page 67, the product being treated either directly with water, or first with sulphuric acid, and then with water; or the roasted mass is sometimes treated with hydrochloric acid for obtaining the copper in a soluble form before lixiviation.

Wet processes have also been proposed by Escalle, Hahner, Henderson, Birkmyre, Gossage, Longmaid, and numerous others; the first three mentioned converting the copper into a chloride before precipitating the copper; and for this purpose M. Escalle calcines the finely-powdered ore in a reverberatory furnace having two beds, the ore being calcined on the one and then drawn forward on to the second, and there treated with hydrochloric acid, when the chlorides so obtained are separated by lixiviation, and the copper precipitated as sulphide by the addition of calcic sulphides (the residues from soda and soap works); when as soon as the whole of the copper is precipitated, and before the other metals are precipitated in sensible amount, the addition of calcic sulphide is discontinued, and the supernatant liquid is drawn off. The cuprous sulphide is then dried, compressed, and smelted with charcoal in a blast furnace.

Hahner and Henderson in their methods propose to convert the copper into chloride by treating the ore with dilute hydrochloric acid, or by heating the ore with sodic chloride (common salt), when ferric, antimonious, and arsenious chlorides are largely volatilised, and from the solution of the chlorides of copper, etc., obtained by treating the residue with water, the copper is then precipitated by barium in the usual manner. Copper and silver are in this manner sometimes separated from the residues left after roasting pyrites for the manufacture of sulphuric acid; the chlorides of copper and silver produced by roasting the pyritic residue with sodic chloride in a reverberatory furnace being dissolved out by treatment with water, since argentic chloride (AgCl), although insoluble in water, is soluble in a

solution of sodic chloride (NaCl), and from this solution the silver is first precipitated as iodide, by the addition of zincic iodide, and the copper in the mother liquor is then separated by treatment with scrap-iron.

The Spanish, Portuguese, and Norwegian pyrites imported into this country yield, after burning for the manufacture of sulphuric acid, *residues* which are treated by the method of Mr. Henderson for the separation of the 4 or 5 per cent. of copper which they contain. The *burnt* residues are mixed so as to contain copper and sulphur in about equal proportions, when from 12 to 15 per cent. of coarsely-powdered *rock-salt* is added to the mixture, which is then ground and sifted.

Charges of about 3 tons of the mixture of ground ore and rock-salt are then carefully *roasted* or *calcined* in reverberatory furnaces, which in the Lancashire works are fired by gas; the calcination being continued for about six hours, or until samples taken from the hearth yield, after treatment with boiling water, a residue which, when boiled with hydrochloric acid and ammonia then added to the acid solution so obtained, affords little or no blue colouration, indicating that the whole of the copper has been converted into a condition soluble in boiling water. By this calcination the sulphur of the ore is oxidized, and if the temperature has been properly regulated, then sodic sulphate with cupric chloride result, both of which are dissolved out in the hot water. The calcination being completed, the charge is now raked from the furnace, and at once introduced into large wooden *lixiviating* vats, provided with false bottoms, and the calcined product is here treated with *hot water* and the *weak liquors* obtained towards the close of a previous lixiviation; for the calcined product receives some eight or nine successive washings, and it is the wash-water obtained in these latter washings that constitute the above weak liquors which are first run into the vats.

The liquors obtained in the above lixiviation, if they contain *silver*, are first treated with a *soluble iodide*, by which the silver is separated as an insoluble iodide, which is allowed to settle, after which the filtrate is conveyed direct to the *precipitating* tanks, which are partially filled with scrap-iron. The *precipitated copper* is separated as completely as possible from the iron with which it is mixed by careful washing,

etc., and by this means the product obtained contains from 70 to 80 per cent. of copper, which is then either smelted for blister copper, or is melted with fine metal and afterwards refined.

Birkmyre roasts the powdered pyrites with sodic nitrate with access of air, and precipitates by metallic iron the copper obtained in solution on lixiviation of the mass.

At Alderley Edge, the ore, consisting of arsenate, carbonate, phosphate, and oxide of copper, disseminated in a sandstone, is treated with crude hydrochloric acid, when the solution obtained by lixiviation of the mass is treated with a salt of iron for the precipitation of the arsenic, which thus falls as arseniate of iron, after which the copper is precipitated by iron plates, the refuse of the manufacture of tin-plate, or old tin plates freed from lead.

28. Cement Copper.--This is the name applied to the copper deposited from the waters of certain mines, when such is brought into contact with plates of iron. Thus the water of the Almrich mine of Anglesea, and the mines of Wicklow, Schmöllnitz, etc., contain cuprous sulphate in solution, and for the extraction of its copper the water is conveyed into pits or tanks containing scrap-iron or iron plates. The water that has fallen upon exposed heaps of copper ores, as well as the water pumped from the mines, is utilised in this operation; and the vats or tanks which, at Anglesea, are about 100 feet in length, with corrugated or furrowed bottoms, are partially filled with old iron, such as tin-plate chippings, and are arranged in terrace form, so that the water flows into the top or head pit, from which it is drawn off after the necessary interval into the second tank, and so on to the end of the series, the number of vats comprised in the series depending upon the quantity of water and the amount of copper it contains. The water is finally drawn off at the end of ten weeks, and the deposited matter is well washed with the water, remaining in the hollows of the corrugations in the vat bottom; while the mud or schlich obtained is passed into pits where it settles into slimes, which, when stiff, are placed on the top of the reverberatory furnace for drying, after which it is passed through sieves, and then melted. The precipitated matter on the floors of the first few pits or vats

is put together as the best, while that from the middle six vats forms the second quality, and that collected from the remaining vats contains only about 5 per cent. of metallic copper, and constitutes the lowest class. In this process, in addition to the copper, an ochreous product is obtained, containing ferric oxide, etc., along with some copper, and which is sold as an ochre. The copper obtained by this process is very pure, possessing a high degree of malleability and ductility.

At Wicklow the water from the mine passes along an inclined channel or trough, across which at intervals are introduced plates of iron over which the waters flow, and deposit the copper from the cuprous sulphate held in solution by the waters; the trough being intercepted at intervals with deep tanks for the deposition of precipitated matters. At Schmöllnitz the water is pumped into a series of precipitating vessels in which cast-iron plates are arranged like lattice-work, the deposition of metallic copper and ferruginous matters occurring in the manner already described.

29. Kernel Roasting.—This is a method of treatment adopted (with ores which are poor in cuprous sulphide, but much richer in ferrous sulphide, and very free from gangue) at Agordo in the Venetian Alps, and elsewhere, for the concentration of the cuprous matters in an inner nucleus or kernel of the pieces of such ore, while the outer crust or shell of the ore, after roasting, consists largely of ferric oxides. For this purpose the ore is broken into pieces of some 2 or 3 inches in diameter, and is roasted either in piles or in kilns. The truncated or pyramidal heaps employed each contain about 200 tons of the ore, which is arranged upon a layer of wood for commencing the combustion, the wood itself resting upon a layer of ferruginous residues from a previous operation, and the whole is covered with a coating of the same matters, or of ore which has been once roasted. After kindling the wood at the corners of the pile, the combustion proceeds slowly, the oxidation of the sulphur in the ore continuing the process for from eight to ten months. When completed, and the pile has cooled, the pieces of ore on examination are found to consist of an outer ferruginous crust, which can be detached by the hammer from an inner nucleus or kernel of copper.

regulus, consisting of the sulphides of copper and iron; the kernels forming from 12 to 15 per cent. of the original volume of the ore, and containing from 4 to 5 per cent. of copper, while the original ore contained only about 1·5 per cent. of copper.

The *kernels* are smelted in small cupola blast furnaces, along with other richer ores, containing from 4 to 8 per cent. of copper, the metal being subsequently refined; while the *crusts* or *shells* are treated with water for the extraction of any cuprous sulphate which they contain, the residues after this treatment constituting when dried the matters which, as already noted, form the first layer at the base, as also the covering of the heaps or piles, such matters after the second roasting in this manner being again lixiviated, and a further proportion of cuprous sulphate extracted therefrom, the metal thus separated being precipitated from the solution by treatment with metallic iron. In this process a large proportion of the sulphur in the ore is lost, only a small proportion, and that mostly in the earlier stages of the operation, being collected as it sublimes from the various points in the surface of the pile.

In the more modern practice adopted in kernel roasting, the ore is roasted in kilns, figs. 13 and 14. These are rectangular chambers enclosed by four walls, in which are cavities *c c*, each communicating with the interior by nine channels, which serve for the collection of sulphur during the roasting operation. Along the sides and at the corners of the kiln also are channels *a a*, communicating with small receptacles *b b*, for the collection of any sulphur collecting on the bed of the kiln. The bottom of the kiln consists of a series of low pyramids, which divide it into a number of compartments, the apices of the pyramids being situated along the median line of the kiln; while along the edges and sides of these pyramids are gutters communicating with others leading to the exterior, and these serve for distributing the air throughout the mass, as also for the collection of sulphur. The front wall of the kiln is taken down and rebuilt at each withdrawal and introduction of the charge. These kilns roast about 3 tons of ore at a time, the charge, in alternate layers of large and small ore, being introduced into the kiln

after having previously inserted at the corners a quantity of wood for commencing the combustion; and at the apex of each pyramid on the bed of the kiln, a sort of perforated chimney is erected with the larger pieces of ore, which thus communicates with the different parts of the mass of the charge, and distributes the air more uniformly throughout the kiln.

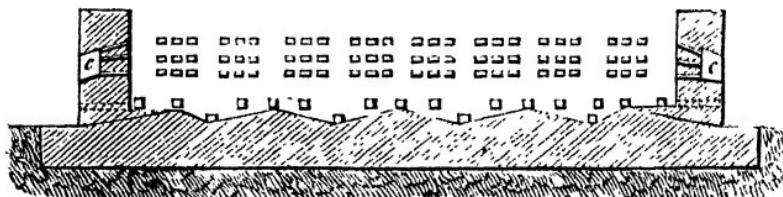


Fig. 13.—SECTIONAL ELEVATION OF KILN FOR KERNEL ROASTING.

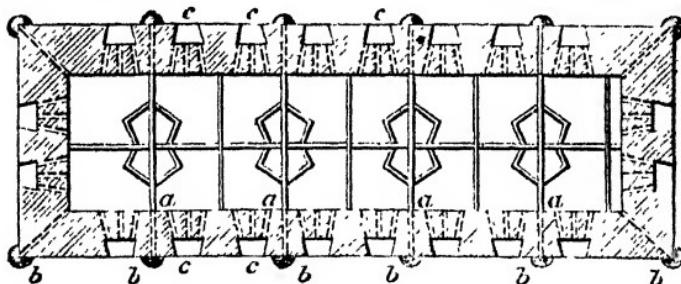


Fig. 14.—HORIZONTAL SECTION OF THE KILN EMPLOYED IN KERNEL ROASTING.

The roasting in kilns occupies from five to six months for its completion, and is attended with the collection of a larger proportion of the sulphur than occurs when roasting in piles is adopted; but the yield of kernels or concentrated regulus is much the same as that resulting from the treatment of the ore in piles. While the pieces of roasted ore are treated in exactly the same manner as in the last method, viz., separation and smelting of the kernel, and lixiviation of the crust or rind.

Pieces of the ore, examined in the earlier stages of this process, exhibit on breaking across a thin external layer resembling ferric oxide, then a shell of matter like copper pyrites, within which is a nucleus of unchanged ore. At the

middle stage of the process, the ore shows on fracture an inner nucleus of unchanged ore, enveloped in a layer possessing a somewhat metallic lustre, and resembling purple copper ore; and outside of which is a layer having the appearance of copper pyrites, while externally is the crust of ferric oxide. In the concluding stage of the process the concentration is complete, and the pieces of ore exhibit a nucleus of a concentrated copper regulus, enveloped in an outer crust or shell of ferruginous matter.

30. Loss in Copper Smelting.—The loss of copper incurred in smelting by the Welsh process must be considerable, since the ore-furnace slag contains about 0·5 per cent. of copper, while the bottoms of the ore furnace, metal furnace, and roasting furnace, as also the refinery absorb considerable quantities of the metal, which is, however, to a large extent, subsequently recovered; in addition to which there is a small loss occurring in the copper rain, and in the particles of copper carried over in the smoke.

By smelting copper in the blast furnace, as practised in Sweden, the loss, which amounts to .25 per cent. of the weight of ore operated upon, is to be found chiefly in the ore-furnace slag, while in kernel roasting the loss amounts to about 7·214 per cent., or $\frac{1}{14}$ th of the total amount of copper in the ore.

CHAPTER II.

LEAD.

31. Properties.—Lead is a bluish-grey, tasteless metal, which emits a peculiar odour when rubbed, and which may be cut by the knife, or scratched by the nail. The freshly cut surface presents a metallic lustre, but its brilliancy disappears very quickly when exposed to the atmosphere, owing to the formation of a film of plumbous suboxide upon its surface; it also leaves a grey streak upon paper. Lead is both *malleable* and *ductile* at the ordinary temperature, being placed sixth in order of malleability* of the metals, and ninth in the order of ductility; but these qualities are very materially influenced by the presence of impurities, as plumbic oxide, etc., in the metal; and also the metal is considerably more ductile after rolling, than it is in the cast state; while in *tenacity* this metal is very inferior, a wire $\frac{1}{12}$ th of an inch in diameter breaking under a load of 20 lbs.; yet it is tough and flexible, and may be bent backwards and forwards without emitting any sound under the treatment; and when gently heated, the metal may be squirted, upon the application of pressure, into the form of hollow tubes or solid rods. Lead emits a dull sound when struck with the hammer, but if cast in the form of a spherical segment it becomes somewhat sonorous. It crystallises in octahedra, while if heated to a temperature just below its melting point it becomes brittle, and assumes the columnar structure like tin under like conditions. The specific gravity of lead at $0^{\circ}\text{C}.$ is given by Kupfer as 11.3303, and by Berzelius as 11.445; while all metals alloyed with it tend to lower its density. Its specific heat between 0° and $100^{\circ}\text{C}.$ is .0314 (Regnault), and its dilation by heat is .000030005 per unit of length for each

* Vol. I., p. 11.

degree between 0°C. and 100°C. It melts at a temperature of about 326°C. (618·8°F.), and is not adapted for taking casts, etc., of objects, since it contracts on solidification and cooling; its latent heat is 5·369. Lead is not sensibly volatilised below a white heat, when heated in closed vessels out of contact with the atmosphere; but with the access of air, fumes of plumbic oxide are sublimed at a bright red heat; and the metal, if obtained in a very fine state of division, is pyrophoric. It is a very inferior conductor of heat and electricity. Two clean surfaces of the metal, when presented together and pressure applied, adhere or become welded; and in like manner, lead, in a fine state of division, may be welded into a solid mass by applying pressure in a suitable apparatus; in like manner, if a perfectly clean sheet of lead and another of tin be rolled together, a compound plate results in which the constituent sheets are apparently welded together. Lead in the massive state is unacted upon by dry air or oxygen at the ordinary temperature, but in moist air the metal is quickly tarnished, and if heated to bright redness, it is rapidly oxidized.

If lead be boiled with water containing free oxygen, the water quickly affords an alkaline reaction; but if the water be void of dissolved oxygen, then it is without action upon lead; in this manner, when lead is exposed to the combined action of water and air, the metal is oxidized, and the oxide so formed is dissolved in the water, from which it is deposited as an hydrated carbonate by the absorption of carbonic anhydride from the atmosphere, so that lead exposed to these conditions is subjected to a gradual corrosion. The presence of chlorides and nitrates promote this action, while sulphates, phosphates, and carbonates exercise a preservative influence upon lead; but water containing much carbonic anhydride is especially destructive upon lead, and therefore dangerous for domestic use after exposure in leaden vessels, since such water converts the plumbic carbonate first produced into an acid carbonate which is soluble in water.

Nitric acid dissolves lead even in the cold with the production of plumbic nitrate and the evolution of nitric oxide; while concentrated sulphuric acid, if heated to the boiling point, converts the lead into plumbic sulphate with the libera-

tion of sulphurous anhydride; but the weak acid in the cold is almost without action upon the metal. Hydrochloric acid has little or no action upon the metal, but acetic acid, or its vapour, in the presence of the atmosphere, rapidly attacks lead. When lead is heated with cupric oxide, the latter is reduced to the state of cuprous oxide with the oxidation of the lead. The chemical symbol of lead is Pb, and its atomic weight is 207.

Commercial lead is frequently almost pure, yet small quantities of silver, copper, antimony, tin, and sulphur, with occasionally iron, arsenic, zinc, and manganese are present in it; the impure lead being usually somewhat whiter and less soft than pure lead, while these impurities are also injurious in its application to the manufacture of white-lead, as in other of its technical applications.

The more important applications of this metal to the arts and manufactures are for the production of sheet-lead and lead pipes, the former employed by the architect as a material for the protection of roofs, the lining of water tanks, sulphuric acid chambers, etc., while the pipes are of universal application for conducting and distributing water or other liquids over different areas; and also owing to its comparative immunity from action by atmospheric influences, it is adopted in the form of wire for certain horticultural applications; while this metal is extensively employed in the manufacture of a series of important alloys, as shot, Britannia metal, etc.

32. Lead and Oxygen.—Lead combines with oxygen in several proportions, yielding plumbous and plumbic oxides, plumbic peroxide, and mixtures or combinations of these three; of these *plumbic oxide*, *massicot*, or *litharge*, and the oxide constituting *minium* or *red-lead*, are of considerable metallurgical importance. All the oxides of lead are reduced to the metallic state upon heating to redness with charcoal.

Plumbous oxide or *suboxide* of lead (Pb_2O) results as a dull black powder when plumbic oxalate is cautiously heated without access of air. It takes fire when heated in the air; and is rapidly oxidized with the formation of plumbic hydrate, when the moistened oxide is exposed to the atmosphere. The grey film mentioned as forming upon the

freshly cut surface of metallic lead, is stated by Berzelius to consist of plumbous oxide.

Plumbic oxide, massicot, or litharge (PbO) *may be obtained by heating plumbous nitrate, carbonate, or oxalato in contact with the atmosphere, at a temperature insufficient to melt the oxide produced, when massicot results as a lemon yellow powder.* This oxide also occurs native as lead ochre, but on the large scale, the products known commercially as *litharge* and *massicot* respectively, are prepared by freely exposing molten lead to the oxidizing influence of the atmosphere, whereby, if the temperature be maintained below the melting point of the oxide so produced, then there results a yellow powder constituting "*massicot*"; whereas, if the temperature be raised sufficiently high to melt the resulting oxide, then it assumes the form of a yellow or reddish-yellow crystalline mass, known as "*litharge*"; which two products, though differing widely in certain physical qualities, are yet identical in chemical composition. An impure litharge results as described on p. 274, during the English and German methods of cupellation. The manufacture of *massicot* is conducted by melting lead upon the flat hearth of a kind of reverberatory furnace or oven, which is maintained at a low red heat, while the film of oxide, or *massicot*, is removed from the surface of the molten metal as rapidly as it is produced; after which the product so collected is freed by grinding and subsequent levigation in the manner described on page 78, from any metallic lead which it may retain. The *litharge* obtained from the cupellation furnace is often very impure, being contaminated with ferric oxide, cuprous and cupric oxides, silica, antimonious oxide, etc., derived from the crude argentiferous lead under treatment.

Plumbic oxide may be obtained amorphous or in distinct crystalline forms, whilst its colour depends upon its state of aggregation, as also if previously fused, whether the cooling has been effected slowly or rapidly; since it assumes a reddish-yellow colour if cooled slowly, while rapid cooling tends to produce the yellow variety; and litharge, when reduced to a fine powder as by grinding, assumes a buff* colour, while in heating to redness, litharge passes through various shades of

* Percy, Metallurgy, Vol. I.

red and purple, but recovers its yellow colour upon cooling. Litharge melts at a red heat to a clear, transparent, orange coloured liquid, which rapidly permeates and destroys earthen crucibles; it is a powerful base, and constitutes the salifiable oxide of lead, it also dissolves in potash, or soda, and in barytes or lime water. This oxide is reduced even at dull redness by carbon, coke, carbonic oxide, hydrogen, or cyanogen; and since plumbic oxide is one of the easily reducible oxides, the temperature required for its reduction by carbon, being below that at which *carbonic anhydride* is reduced to *carbonic oxide* by contact with carbonaceous matters; it hence follows that carbonic anhydride and *not carbonic oxide* is evolved in its reduction by carbon. When exposed at a low red heat for a considerable time with access of air, the plumbic oxide is converted into the higher oxide, known as minium or red-lead. Litharge, when heated with many metallic oxides, yields fusible compounds, although these oxides when heated alone may be perfectly infusible; thus fusible products are obtained by heating litharge with iron scales, ferric oxide, manganous oxide, stannic oxide, etc.; but these various oxides require different proportions of litharge to effect their fusion, thus plumbic and cuprous oxides in equivalent proportions yield a very fusible product which rapidly attacks the crucible in which it is heated. Ferric oxide in like manner requires four times its weight, zincic oxide eight times, and stannic oxide from twelve to thirteen times its weight of plumbic oxide to effect its fusion. Arsenious anhydride also melts with plumbic oxide, yielding a characteristic waxy-looking brown-yellow compound; and, if heated with sulphur in not too large proportion, litharge acts as an oxidizing agent, evolving sulphurous anhydride, and liberating an equivalent of lead, without any plumbic sulphate being produced. Litharge also acts as an oxidizing agent when heated along with various metals, yielding an oxide of the metal with the separation of more or less metallic lead; such a reaction occurring when copper, zinc, and notably iron are the subjects of operation.

Plumbic hydrate, or the hydrated plumbic oxide, is prepared by adding a solution of the neutral plumbic acetate to an excess of ammonia, when this compound falls as a

white precipitate, rapidly absorbing carbonic anhydride if exposed to the atmosphere; it gives up its water on the application of heat, yielding the anhydrous oxide. If potash be used instead of ammonia as the precipitant, the precipitated oxide is always mixed with more or less basic salt of lead.

Red oxide of lead, red-lead or minium (Pb_3O_4) results as above stated on the oxidation of plumbic oxide, and on the large scale it is manufactured by exposing lead at a low red-heat upon the hearth of a reverberatory furnace to the oxidizing influence of air; when the *massicot* so produced is ground and levigated for the separation of metallic lead and coarser portions, after which it is again exposed to further oxidation in a similar furnace for the production of red-lead. This oxide being extensively employed as a pigment, and for the manufacture of glass, etc., is hence an article of commercial manufacture, and the method pursued on the large scale will be described in the next article. The red oxide also occurs native, associated with other lead ores. Red-lead is a bright or orange-red crystalline or granular powder, of which the tint varies much according to the method adopted and care observed in its manufacture; upon the application of heat it darkens in colour, and becomes eventually purplish or black, recovering however its original colour on cooling, unless the temperature has been urged to strong ignition, when this oxide is resolved into plumbic oxide (litharge) and oxygen gas. Its specific gravity is 8.62 (Karsten); it is insoluble in water, and is a bad conductor of heat and electricity. When heated with concentrated sulphuric acid, oxygen is evolved, and a residue of plumbic sulphate remains. A small quantity of hydrochloric acid decomposes it with the production of plumbic chloride, plumbic peroxide and water; thus,



while a larger proportion of hydrochloric acid liberates chlorine with the formation of plumbic chloride and water,



Nitric acid converts it into the soluble plumbic nitrate, and a residue of plumbic peroxide.

Plumbic peroxide, puce oxide (PbO_2) results as above noted on the digestion of the red oxide with dilute nitric acid, when the oxide remaining after the decantation of the nitrate, requires washing with boiling water; it is also prepared by suspending plumbic oxide (PbO) in water, through which a current of chlorine is passed, and in a number of other ways. It also occurs native as Plattnerito. The artificial oxide is a brown or puce-coloured powder, which is decomposed by heat into the red oxide, or if the temperature be increased to redness, then plumbic oxide is formed, in either case attended with the liberation of oxygen; when rubbed with sulphur it is spontaneously inflammable, burning with a bright flame, and yielding plumbic sulphide. Plumbic peroxide mixed with sulphur is a constituent of the mixture employed in tipping certain matches. This oxide combines with strong bases as potash, when boiled with them, forming a class of unstable compounds known as *plumbates*, the plumbic peroxide thus appearing to play the part of a weak acid, and is, accordingly, sometimes called *plumbic acid*.

33. Manufacture of Red-Lead. — This manufacture is extensively pursued in Derbyshire, etc., for the production of red-lead for use as a pigment, and in the manufacture of glass. The manufacture involves two stages, conducted either in the same or similar furnaces or ovens. The first or *drossing* stage operates upon charges of from 1500 lbs. to 2000 lbs. of pure lead, and if the product be only intended for glass making, about $\frac{1}{5}$ th of its weight of hard lead is added; but if for a pigment where purity of colour is especially desirable, then only pure lead is operated upon, since small quantities of iron, antimony, or silver in the lead impairs the brilliancy and purity of the colour; and such metals also yield an inferior product for the glassmakers' use, imparting an undesirable dulness to the glass. The lead for oxidation is placed upon the bed or hearth of a low arched reverberatory furnace or "drossing oven," which is everywhere closed except at the front end, through which the charge is introduced, rabbling conducted, and the product finally withdrawn. The bed of this oven is formed of brick, supported upon a bed-plate of cast-iron, and inclines slightly towards the median line; whilst a line of bricks, running from back

to front along each side at a little distance from the side walls, forms two long fire-bridges, between which and the outer walls are the two fireplaces, which, in some furnaces, are supplied with fire-bars, whilst others are without bars; and the fuel consumed may be either coal or coke. The charge is retained upon the bed of the oven at its front end, by a dam formed of the residues of lead and plumbic oxide obtained in the levigation of a previous product, and which is rammed as a barrier across the bed, between the two fire-bridges. The drossing chamber and its two fireplaces can be closed at the front or near end by separate doors, and a hook is likewise suspended in front for the support of the rabbelling bar during the working of the charge; and also at the front end is built a hood, supporting a kind of stack for carrying away the gaseous products, etc.

When the lead is melted it is continuously rabbled, especially during the earlier stages of the oxidation or *dusting*, as it is called, so as to bring fresh portions of the metal under the influence of the oxidizing atmosphere maintained in the oven; at the same time, the temperature is carefully regulated so as not to exceed low redness, preventing thereby the fusion of the *massicot* or *dross* produced in this stage. The dross, as it forms, is pushed from the surface of the metal to the back of the oven; while on to the heap so formed the workman projects the molten lead, at intervals, so as to expose the metal more completely, and thus expedite the oxidation. After about twenty-four hours the drossing stage is completed, and the metal appears to be wholly converted into oxide. The front dam is then broken down in order that any metallic lead may be allowed to drain out from the mass, while the massicot, after remaining for some time so as to cool, is raked out into a receptacle at the front and moistened with water, when another charge of lead is introduced into the furnace, and the drossing operation just described is repeated; or otherwise the ground and levigated massicot, from a previous charge, is introduced into the same furnace to undergo the last or colouring stage.

The massicot or dross having cooled, is now ground under edge stones to the state of fine powder, which is then levigated or washed in a suitable apparatus, whereby the finely-divided

massicot, which is of a yellow colour, is carried in suspension by the water passing through the apparatus and deposited in the settling or depositing vessels, from whence it is collected, and after drying is returned for the next or colouring stage of the process; whilst the coarser and heavier particles, with any metallic lead still unoxidized, are left as a general residue in the apparatus, and this residue is employed to form the dam across the front of the drossing furnace hearth.

The *colouring* is either conducted in the same oven as the previous stage, or a second furnace known as the *colouring oven*, not however materially different in construction to the last or drossing oven, is retained for the concluding stage. In either case the massicot or dross is placed upon the bed of the furnace, and carefully heated to a temperature somewhat below that employed in the drossing stage, or between 287.7°C. (550°F.) and 317.1°C. (600°F.), at which heat it is kept well exposed to the atmosphere, by continued rabbling or stirring for a period of forty-eight hours, or until a sample taken from the hearth appears while hot, of a dark red colour, changing to a bright red on cooling; upon which the furnace is closed and left to cool slowly, the latter condition being considered essential to the success of the colouring stage; after which the product is drawn from the oven, and only requires grinding and sifting to prepare it for the market.

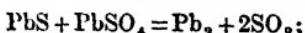
Commercial red-lead is frequently adulterated with brick dust and ferric oxide, but these impurities are readily detected by strongly heating the compound; upon which the pure red-lead assumes a yellowish tint, while the brick dust and ferric oxide retain their red colour.

34. Lead and Sulphur.—Lead and sulphur readily combine under the influence of heat; and if sulphur be added to melted lead, combination ensues with the production of plumbic sulphide (PbS), the whole mass being raised to redness by the heat produced. Four sulphides of lead are described, but only one, *plumbic sulphide*, is of metallurgical importance.

Plumbic sulphide (PbS), as occurring native, constitutes "galena," the most abundant and important of the ores of lead, being that from which the metal is chiefly extracted. Plumbic sulphide is prepared artificially, as above stated,

when sulphur is added to molten lead; also by heating plumbic oxide with an excess of sulphur. As obtained by these methods it forms a lead or bluish-grey, brittle, granular body, which melts at a strong red heat, and at a higher temperature may be sublimed, if the access of air be prevented; but if very gently heated in contact with the atmosphere, as in roasting galena, then plumbic sulphate, with plumbic oxide and a little metallic lead remain behind, while about one-half of the sulphur is removed as sulphurous anhydride; whilst if the temperature be increased, the plumbic sulphide and oxide contained in the roasted mass decompose each other, with the production of metallic lead and sulphurous anhydride—

If plumbic sulphide be heated in the vapour of water, it yields sulphuretted hydrogen and plumbic oxide—the latter then reacting, as above, upon the plumbic sulphide, with the production of sulphurous anhydride, plumbic sulphate, and metallic lead. And when plumbic oxide and plumbic sulphide are heated together, if the latter be in excess of that required for the production of metallic lead and sulphurous anhydride, according to the above equation, then the excess of plumbic sulphide separates as such; or likewise, if the plumbic oxide be in excess, it then remains undecomposed, forming a layer above the separated metallic lead. Again, if plumbic sulphide and plumbic sulphate be heated together in such proportions that the sulphur and oxygen are present in the ratio required for the production of sulphurous anhydride, then a double decomposition ensues, metallic lead being separated, while sulphurous anhydride is evolved, thus—



and these reactions between plumbic sulphide and plumbic sulphate and oxide constitute four important chemical decompositions involved in the smelting of lead.

When plumbic sulphide is fused with an alkaline carbonate, and *iron nails* or *scrap iron* is added, the whole of the lead is reduced to the metallic state, while without the addition of the iron, but one-half of the metal is reduced; and the reducing

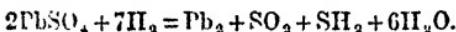
action of alkalies or alkaline carbonates is also further promoted by the addition of *free carbon* to the charge. *Plumbic sulphide* is completely reduced by metallic iron at a red heat with the production of ferrous sulphide; but it is important for the complete reduction of the plumbic sulphide that the temperature employed be sufficient to melt the ferrous sulphide produced; and this method for the reduction of lead is practised in the laboratory for the assay of lead ores, and also on the large scale in Bohemia, the Hartz, and elsewhere, in the smelting of lead, by what is known as the iron reduction process. Metallic lead is not separated when plumbic sulphide is heated with *ferric oxide*; but if carbon be introduced with the mixture, by which the iron is reduced from the ferric oxide, then metallic lead separates as in the previous case. Copper also, when heated with galena, reduces a portion of the lead, the products being a regulus of lead and copper, beneath which separates a stratum of lead also containing a little copper. *Potassic cyanide*, when heated with plumbic sulphide (galena), reduces the greater portion of the lead with the production of a potassic sulphocyanide, and by repeated heating with potassic cyanide, the whole of the lead may be separated in the metallic state.

Plumbic sulphide is insoluble in the cold dilute acids; but if boiled with *dilute nitric acid*, it is dissolved with the formation of plumbic nitrate and the evolution of nitric oxide, whilst the sulphur is precipitated in the form of yellow oily drops; but the finely-divided sulphide, when treated with *concentrated nitric acid*, is wholly converted into plumbic sulphate. Concentrated *hydrochloric acid* also decomposes plumbic sulphide with the formation of plumbic chloride ($PbCl_2$) and the evolution of sulphuretted hydrogen.

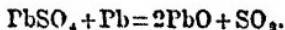
An *hydrated plumbic sulphide* is precipitated as a black or brownish-black precipitate, when sulphuretted hydrogen or an alkaline sulphide is added to a solution of a salt of lead, or when the first mentioned is passed through water in which an insoluble compound of lead is suspended.

35. Lead with Sulphur and Oxygen.—Plumbic sulphate ($PbSO_4$) falls as a heavy white amorphous powder when sulphuric acid, or a soluble sulphate, is added to a solution of a soluble salt of lead; and, as previously stated, it is formed,

attended with the liberation of oxygen, upon the treatment of red-lead, or plumbic peroxide, with sulphuric acid; and it is also slowly produced when sulphuric acid is boiled with metallic lead, whilst as the mineral "*Anglesite*," it occurs native in the crystallised state. Plumbic sulphate is almost insoluble in pure water, requiring about 31,000 parts of water at 15°C. to dissolve it; but it is somewhat soluble in strong sulphuric, nitric, or hydrochloric acid. It is decomposed, with the deposition of plumbic carbonate, upon boiling with a strong solution of potassic or sodic carbonate. Plumbic sulphate melts at a red heat, and if not in contact with silicious matters, the fusion is effected without decomposition; but when heated with plumbic sulphide it yields metallic lead, as explained in the last article; it also yields metallic lead upon heating in a current of hydrogen, thus—



When heated with *carbon* it yields metallic lead, and plumbic oxide or plumbic sulphide, according to the proportion of carbon employed; but if heated with *metallic iron*, then the whole of the lead is reduced to the metallic state. Plumbic sulphate is decomposed when heated to redness with potassic or sodic carbonate, or lime, yielding an alkaline sulphate along with plumbic oxide; but if potassic cyanide be substituted for the carbonate, then the lead is wholly reduced to the metallic state. *Silica* also decomposes plumbic sulphate at a red heat, with the production of plumbic silicate, and the liberation of sulphuric anhydride (SO_3) or sulphurous anhydride (SO_2) and oxygen; while lead heated with plumbic sulphate in equivalent proportions, yields a residue of plumbic oxide and liberates sulphurous anhydride, thus—



It has been proposed to substitute this compound in lieu of white-lead in painting, as not being so injurious to the health of the workman, but from its crystalline and translucent character it does not give the body and opaque whiteness which is afforded by white-lead. It is also rapidly blackened by sulphuretted hydrogen, as are all the other salts of lead.

86. Lead and Phosphorus. — These elements combine

directly when phosphorus is projected upon melted lead. A phosphide of lead is also produced when lead filings are ignited with glacial phosphoric acid, the resulting compound having the colour of lead, retaining also its softness, but tarnishes quickly on exposure to the atmosphere.

Various phosphates of lead may be obtained by the precipitation of a soluble salt of lead, by the various forms of sodic phosphate under different conditions; and a phosphate of lead also occurs native as the mineral "*Pyromorphite*." The whole of the phosphates are insoluble in water, and all are reduced to the metallic state upon strongly heating with charcoal (Percy); but are not reduced by plumbic sulphide.

37. Lead and Arsenic.—Lead and arsenic alloy together, as when arsenious anhydride (As_2O_3) and molten lead are brought into contact, in which manner arsenic is added to lead intended for shot-making, the addition of arsenic causing the globules of metal to assume a more perfect spherical form. Arsenic has the effect of rendering lead, greyer in colour, harder, more brittle, less malleable, and more fusible.

38. Plumbic Carbonate: White-Lead.—When lead is exposed to the influence of oxygen, carbonic anhydride, and moisture, as on exposure to ordinary atmospheric influences, then the metal becomes coated with a white, *amorphous, flaky*, weakly adherent coating of an hydrated plumbic carbonate, which differs, however, both in composition and physical characters from the plumbic carbonate obtained by the precipitation of a lead salt by an alkaline carbonate, inasmuch as the latter is always *crystalline* and somewhat *translucent*. Hence it is much inferior as a material for use as a pigment, to which these carbonates are applied under the name of "*white-lead*" or "*flake white*," since the precipitated carbonate does not afford the opaque whiteness, or body, which is given by the product obtained by the direct action of carbonic anhydride upon plumbic hydrate, as produced in the first-mentioned method; and accordingly the methods of manufacture employed for the production of *white-lead* for the use of the painter, though differing somewhat in detail from one another, are yet all processes in which the product results from the absorption of gaseous carbonic anhydride.

Plumbic carbonates behave like plumbic oxide on heating in contact with the atmosphere, yielding thereby a variety of red-lead having an orange tint, and hence known as *orange lead*.

The substance known as *white-lead*, *ceruse*, or *flake white*, is a highly basic plumbic carbonate, or is plumbic carbonate with plumbic hydrate, and for commercial purposes it is manufactured according to one of the two following methods: the older, known as the *Dutch method*, and which yields an excellent product, consists in exposing lead to the combined action of carbonic anhydride, the vapour of water, acetic acid, and atmospheric air, aided by a very gentle heat. For this purpose plates of lead and trellis-like castings of the metal are introduced into and upon a series of pots arranged in rows upon a layer of tanner's spent bark, placed upon the floor of a large brick or stonework chamber, the pots which are of two sizes being placed in regular sequence—several rows of the smaller between each row of the larger; whilst upon a flooring of wood resting upon the tops of the taller pots is placed another layer of bark or stable litter, then a series of pots as before, and so on in succession until the chamber is filled, the last rows or tier of pots being covered with bark, and the whole constituting what is known as a *stack*. Into each pot is placed a small quantity of very dilute acetic acid above which in the larger pots is suspended a coil of lead, while upon the top of the smaller vessels is placed a series of the trellis-like castings of lead until the height of the larger pots is attained. By this arrangement the heat from the litter or bark, together with that produced by the oxidation of the lead affords the necessary warmth, whilst the litter also supplies carbonic anhydride to the mass, and atmospheric air has access to all parts of the stack; so that the conditions stated above are fulfilled, and in from two to four months the lead has become wholly converted into white-lead, when the stack is taken down, and after *grinding*, *washing*, *levigating*, and *drying*, the product is ground in oil and is then ready for the market.

The second method pursued in the manufacture of white-lead consists in passing carbonic anhydride through a weak solution of plumbic acetate, in which plumbic oxide (litharge)

is suspended; or by passing the same gas through a solution of a basic plumbic acetate.

White-lead is also manufactured according to what is known as the *German method*, in which the vapours of acetic acid and of water are passed into a chamber containing thin plates of lead, and subsequently air and carbonic anhydride are admitted.*

Commercial white-lead is frequently mixed with heavy-spar, gypsum, zincic oxide, etc., these bodies being unaltered by exposure to an atmosphere containing sulphuretted hydrogen, and therefore rendering the white paint less liable to be discoloured from this cause. Sometimes also finely-divided metallic lead occurs in white-lead, when the sample acquires a more or less grey colour.

39. Lead and Silica.—Silica melts easily when heated with plumbic oxide or with red-lead, with the formation of a yellow glass of plumbic silicate, of which the composition varies with the proportions of silica and plumbic oxide present; for silica forms several definite silicates by union with plumbic oxide, besides yielding fused masses of plumbic silicate containing also probably an excess of either silica or plumbic oxide. Also the larger the proportion of plumbic oxide, the deeper is the colour of the resulting silicate, while the fusibility of these silicates decreases with an increase in the proportion of silica present. Plumbic silicate is only very imperfectly reduced upon strongly heating with charcoal; Dr. Percy adding,† that after reduction has proceeded to a certain limit, a more or less infusible body, containing plumbic oxide and silica, is produced, but which substance is unaffected upon by charcoal even at a white heat, and hence a portion of the lead escapes reduction; but the *lead is wholly reduced from all its fusible silicates when heated along with metallic iron*; and the same result is effected if the plumbic silicate be heated with charcoal and ferric oxide. When the plumbic silicate ($2\text{PbO}, \text{SiO}_2$) is heated with sulphur, only a small proportion of lead is reduced; but this silicate is largely, though yet very imperfectly, reduced upon heating with lime and charcoal.

* Dingl. polyt. J.

† Percy. *Metallurgy*, Vol. III.

The compound silicates of lead and potash, soda, or lime, constitute the different varieties of glass known as potash, soda, or lime glass; the first mentioned being characterised by a high lustre and greater refractive power than the other varieties, and is hence used as an optical glass, whilst the soda and lime glasses are frequently tinged also with a greenish tint. The refractive power of glass also increases with the proportion of plumbic oxide present in the silicate.

40. Alloys of Lead.—Lead may be alloyed with several of the more common metals by simple and direct fusion, as with *antimony* in the production of *type-metal*, which alloy consists of eighty-three parts of lead with seventeen parts of antimony, to which, for the production of stereotype plates, is added in addition a considerable proportion of tin (see Vol. I. p. 211 and 219). Some of the alloys of lead are of considerable and extensive application to the arts, thus lead is a constituent of an inferior variety of Britannia metal known as "*Queen's metal*," applied in Birmingham to the manufacture of jugs, tea-pots, etc.; it also enters into the composition of *pewter*, *plumbers' solder*, etc., as will subsequently appear.

The alloys of *lead* and *antimony* are harder and more fusible than either metal alone, and are also more oxidizable than lead; but the alloy containing three parts of lead to one of antimony, although harder than lead, has not acquired the brittleness of zinc or bismuth, while equal proportions of the two metals yield a porous and brittle alloy. The alloys of lead and antimony have several applications to the purposes of the arts.

Arsenic, as already stated, renders the metal more fusible, greyish-white in colour, and more brittle, while for the purposes of shot it gives to the globules the quality of assuming a more truly spherical form. For this last application from 30 to 40 lbs. of arsenic is added per ton of lead, and either metallic arsenic or arsenious anhydride (As_2O_3) may be employed for the purpose, the arsenic being introduced into the lead kept molten in a suitable pot, the surface of the metal being partially covered with charcoal during the operation.

Homogeneous alloys of *copper* and *lead* can only be obtained with difficulty; for if the alloy of these metals be

heated just above the melting point of lead, yet sensibly below that of copper, then lead containing a little copper liquates out from the mass, leaving a porous residue of copper retaining a small proportion of lead; and this is the principle of the old liquation process for the extraction of silver from argentiferous copper, according to which the copper was first alloyed with lead and then subjected to liquation, by which the lead, carrying with it the silver, was liquated or sweated out from the alloy. In the preparation of the alloy of these two metals, it is hence necessary that the copper be introduced into the melted lead, and that the mixture be well stirred during the incorporation, when the alloy so obtained is rapidly cooled to prevent the separation of the two metals. Lead in very small proportions suffices to impair the ductility and malleability of copper, both at ordinary temperatures and at a red heat.

Mercury may be readily alloyed or amalgamated with lead, simple trituration of lead filings with metallic mercury sufficing to effect the amalgamation, and the union may also be effected by introducing mercury into molten lead. The resulting amalgam has a white colour, and with one part of lead to two parts of mercury, the mercury still retains its liquidity.

Lead and *tin* by their union afford alloys, as pewter, various solders, etc., which have an extensive application to the arts. These metals admit of fusion together in all proportions, and the resulting alloys have a somewhat darker colour, with less brilliancy than tin, they are also generally harder and tougher than the latter metal, and wares of the alloys of these metals, like pewter, etc., may be fashioned either by casting to form or by hammering. *Pewter*, as used for the manufacture of spoons, etc., is an alloy of 80 per cent. of lead with 20 per cent. of tin; but other metals, as copper, antimony, and zinc, are frequently added for special purposes, a little copper rendering the alloy harder and more sonorous. *Plumbers' solder*, as above stated, is an alloy of these metals, containing, in *coarse solder*, two parts of lead to one of tin, while *common solder* is formed of equal parts of the two metals, and *fine solder* contains two parts of tin to one of lead, the melting point of the alloy increasing as the proportion of lead is increased. An

alloy of these metals, along with bismuth, constitutes the alloy melting at 93.75°C (200°F), and known as *fusible metal*.

Zinc may be melted with lead in all proportions, but on cooling, the alloy does not remain homogenous, for the zinc largely separates as an outer crust; whilst if these alloys be maintained in a state of fusion with continual stirring, then the lead has a tendency to concentrate itself in the lower end of the mass, while the upper end becomes more largely zinciferous. The alloys of lead and zinc are decomposed at a white heat with the volatilization of the zinc, carrying along with it a small proportion of the lead. The effect of zinc in lead is to harden the latter without impairing its malleability, while small quantities of lead in zinc renders the zinc inferior for rolling into sheets. As noted above, owing to the lower melting point of zinc than lead, separation of the two occurs on cooling from fusion; and it is further found, that if the lead be argentiferous, then the silver is concentrated in the zinciferous crust, and the lead largely desilverised; so in this manner zinc has been employed for the desilverization of lead by what is known as Parkes' process (see page 152). In like manner, zinc can be employed for the separation of copper from lead; since, in melting the alloy of lead and copper with zinc, then allowing the temperature to fall as before, it is found that an alloy of lead, copper, and zinc separates in the form of a pasty mass, which floats on the surface of the lead, and under proper conditions, the lead will not retain more than some .002 per cent. of copper. The formation of a readily fusible alloy with lead, zinc, and bismuth, has been already noticed.

Silver forms alloys with lead in all proportions, and all lead contains more or less silver, while the affinities of these metals for each other are in constant application to the metallurgical treatment of argentiferous ores and products. The alloys of lead and silver separate when slowly cooled from fusion (Lovel) into an inner core and an outer crust, of which the outer crust is much poorer in silver than the interior of the mass; and, further, the alloy richest in silver remains fluid at a lower temperature than the poorer alloy, so that, by properly regulating the temperature, the richer and poorer portions may be separated; and practical application of this quality is afforded in the *Pattinson process* for the

separation or concentration of silver in the treatment of argentiferous lead. In this alloy also, when melted and exposed to the action of a blast of atmospheric air, as in the process of cupellation, the lead is rapidly oxidized to the state of litharge, while the silver remains unchanged.

Gold may be alloyed with lead in the same manner as silver, yielding thereby brittle alloys; for very small quantities of lead in the gold intended for coinage render it unworkable in the coining process; while, like silver, the gold may be separated from lead by cupellation.

41. Ores of Lead.—Lead occurs as an occasional constituent of a very large number of the ores of other metals, but the minerals containing this metal as an essential constituent, in sufficiently large quantity, and occurring in sufficient abundance to constitute them ores of lead, are exceedingly limited in number, a single ore, viz., "*galena*," furnishing by far the greater proportion of this metal; while the plumbiferous minerals or ores almost always contain more or less silver, and are accordingly described as argentiferous or non-argentiferous according as the proportion of silver is sufficient or otherwise to pay for its extraction. The minerals containing lead, and occurring in sufficient abundance to be classed as ores of this metal, may be placed under two heads—I. Sulphides of lead, and II. Oxycompounds of lead, as the carbonates, sulphates, phosphates, oxides, etc., of lead. But, besides these two classes, there are a number of minerals which, though not of sufficient importance to rank as ores of lead, yet are more or less abundant, and often associated with galena, so that they frequently come under the notice of the metallurgist, and call for a brief description of their qualities in this place.

At the head of the first division of lead ores consisting of the sulphides of lead, occurs "*Galena*," *Plumbic sulphide*, (PbS), or as it is sometimes called "*blue lead*," which is by far the most important and abundant ore of lead, containing when pure 86·61 per cent. of lead, with 13·39 per cent. of sulphur; and which is further a most important source of silver, since silver, as also gold, are probably invariable constituents of all galenas, though in some cases their quantity may be exceedingly small. Galena forms a lead-grey mineral having

a streak of the same colour. It possesses a metallic lustre, a hardness of about 2·5, and a fine, coarsely-granular, or fibrous fracture; and it has been generally considered that the more finely-granular, or, as they are called, *steely* varieties of the ore, are more highly argentiferous than the coarse, large grained specimens; and though a comparison of the galenas of a certain locality will frequently confirm this view, yet, as a general rule applicable to the comparison of a coarse-grained galena from one district with a steely specimen from another, the rule is doubtless erroneous. Galena occurs crystallised in the cubic system, chiefly as cubes and octahedra, and it has a very perfect cubic cleavage. The specific gravity of this ore ranges between 7·25 and 7·7. When heated before the blow-pipe this mineral decrepitates, then fuses, and finally yields on charcoal a globule of metallic lead.

Galena is very widely distributed over the globe, occurring in almost every country, and both in the older and more recent geological formations. Thus it forms veins in the Devonian formation "killas" of Cornwall and Devon, in the carboniferous or mountain limestones of Cumberland, Derbyshire, Flintshire, and the North of England, which formation yields the largest proportion of the British lead ores; while in Cardiganshire, Shropshire, Montgomeryshire, the United States, etc., it occurs in the lower silurian rocks. At Freiberg, again, it occurs in gneiss; in the county Wicklow, in granite; while Sweden affords this mineral in a matrix of granular limestone. In addition to these localities, galena also occurs in Scotland—in the Lead-hills of Lanarkshire,—the Isle of Man, largely in Spain, Germany, and Northern Italy, and in smaller proportions in France and Belgium; it is also found in Siberia, Algeria, and Australia, numerous parts of North and South America, etc.

As above stated, the pure sulphide contains 86·61 per cent. of lead; but galena is very often impregnated with small quantities of other bodies, as *silver*, *gold*, *blende*, *iron-pyrites*, *mispickel*, *sulphide of antimony*, *fahlore*, *ferrous carbonate*, *calamine*, *quartz*, *dolomite* or *pearl-spar*, *barytes*, *fluor-spar*, *calc-spar*, etc.; whilst, more rarely, it also contains manganese, anthracite, etc. The presence of these substances necessarily reduces the percentage of metal in the

ore, so that the ores smelted in England contain on the average from 70 to 80 per cent. of lead; but at Freiberg, ores containing only 40 per cent. of lead are smelted; while, if other metals, as copper, silver, or gold, are present in profitable proportions, the lead in the ores is then extracted and paid for, although its amount may not exceed 15 per cent. The first-mentioned associates of galena, viz., silver and gold, are of constant occurrence in it, probably existing as sulphides. The gold is most frequently, however, in very small proportions, while silver occurs in very varied proportions, but rarely exceeding 1 per cent., while an ore containing .25 per cent., or about 82 oz. of silver per ton, is considered a very rich ore; and ores assaying only about .005 per cent. of silver, and which yield a lead containing not more than 2 oz. of silver per ton of metal, can be profitably treated by the Pattinson process for the extraction of the silver. Besides the above-mentioned associates of galena, the rarer minerals containing lead, such as plumbic carbonate, chromate, phosphate, sulphate, and oxide, are frequently associated with it.

Plumbic sulphide also occurs in combination with sulphide of antimony in the minerals *Jamesonite*, *Boulangerite*, and *Geocromite*, and with cuprous sulphide in addition it constitutes the mineral *Bournonite*.

Of the second class of lead ores or oxycompounds of lead enumerated above, the most important and abundant is the plumbic carbonate, cerussite, or white-lead ore, a transparent or translucent mineral, of a white or greyish colour, with an occasional bluish tinge, possessing an adamantine or vitreous lustre, with a colourless streak, and a hardness of from 3 to 3.5. It occurs in fibrous, compact, or earthy masses, as also in crystals of the trimetric or prismatic system. This ore is found in lodes, as also in beds in limestone, usually associated with galena; and at Aix-la-Chapelle it is raised in considerable quantity, as also in the vicinity of Santander in Spain. It likewise occurs in Cornwall, Devon, Yorkshire, the Lead-hills of Scotland, county Wicklow, Westphalia, France, etc.

Plumbic sulphate or *Anglesite* (PbSO_4) occurs as a white, grey, greenish, and sometimes bluish, translucent, or opaque mineral, having an adamantine lustre, with a hardness of from 2.5 to 3. It occurs in cavities, also in lodes crystallised

in the trimetric or prismatic system, and is often associated with galena and plumbic carbonate, at Anglesey, in Scotland, Cumberland, Derbyshire, Hartz, Spain, Germany, France, and the United States. This compound, combined with cuprous carbonate, etc., constitutes *Caledonite*, and a similar mineral is known as *Lanarkite*.

Pyromorphite or *plumbic phosphate* varies in colour between green, yellow, and brown, and has a white or yellowish streak. It usually contains plumbic chloride as well as phosphate, and certain varieties contain also plumbic arseniate. In Derbyshire this mineral is known as "linnets" from its peculiar colour. The mineral also occurs in the Lead-hills of Scotland, in Cumberland, Durham, Yorkshire, Cornwall, Wicklow, Bohemia, Saxony, Hartz, France, the United States, etc.

Minetesite, or plumbic arseniate, is an analogous mineral to the last, but contains arsenic acid, in lieu of phosphoric acid, as an essential constituent. It forms a pale-yellow or brown mineral, with a white streak, occurring at Redruth and other mines of Cornwall; also in Devonshire, Cumberland, Saxony, France, Sweden, South America, etc.

The ores of lead found near the surface often belong to the second class or oxycompounds of lead, and are a result of the decomposition and oxidation of galena.

Besides these sulphur and oxidized ores of lead, numerous minerals containing lead in large proportion occur, but not in sufficient abundance to constitute them ores of lead, of such are *plumbic chloride*, *Mendipite*, *plumbic chromate*, etc.

E EXTRACTION OF LEAD FROM THE ORE.

On reviewing the various methods pursued in the different lead smelting districts of the globe, one is struck by the variety of methods pursued, the various classes of furnaces employed, as well as the difference in fluxes, fuel, etc., employed in each district for the common object of separating metallic lead from its chemical combination, and from the gangue or vein-stuff with which it is associated. Yet it is found, upon further observation, that each one of the various methods pursued and furnaces employed, has usually special

advantages to recommend it for adoption in the particular locality; and that frequently a furnace or method, which in one locality appears to work more satisfactorily, and afford a better result than another working in a different locality, would, if transferred to the new district, and worked under the altered conditions of ore, fuel, and flux, prove an entire failure. The considerations which thus determine the method of reduction to be pursued, and the furnace to be employed in the smelting of the lead ore of any locality are— 1° , the *nature and yield* of the ore to be treated; 2° , the character of the *gangue, matrix, or vein-stuff* with which it is associated; 3° , the nature of the material available for use as a *flux*; and 4° , the *nature and abundance of fuel* in the district.

The processes employed for the smelting of lead ores may be classed according to the type of furnace employed, as— 1° , the methods of smelting in *reverberatory furnaces* as pursued in England, France, and Carinthia; 2° , the methods in which *cupola furnaces* are employed, as practised in the Hartz, Silesia, etc.; and 3° , the methods of reduction in *open hearths*, as in the ore furnace or Scotch hearth, and the American hearth; but Dr. Percy* supersedes these classifications, by grouping the various processes employed for the smelting of galena or other sulphur compounds of lead, under three types, according to the agent employed to effect the decomposition of the ore, and separation of the lead, thus—

I. “*Air-reduction process*,” in which atmospheric air, aided by heat, form the reducing agents.

II. The “*iron reduction or precipitation process*,” in which iron, or an oxidized compound of iron which under the furnace conditions yields iron, is employed for the separation of the lead.

III. The method of “*roasting with subsequent deoxidation of the product by carbonaceous matters*,” while

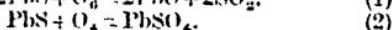
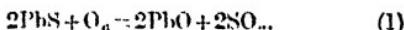
IV. For the smelting of the ores of lead, such as carbonates, silicates, and oxides, in which the metal exists wholly in the oxidized state, it is necessary to reduce the metal either by *carbon* or *iron*; or both of these agents may be employed.

* Percy. *Metallurgy*, Vol. III.

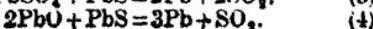
**AIR-REDUCTION PROCESSES FOR THE SMELTING OF
LEAD ORES.**

In the reduction of lead by this process, the reverberatory furnace is extensively employed, examples of which are afforded by the *Flinshire*, the *Flowing*, the *Spanish*, and the *Bleiberg furnaces*, to be described in the ensuing pages; while the process is also conducted in the *ore-hearth*, a species of blast furnace. But the methods of smelting in the Flowing, Spanish, and the Bleiberg furnaces, are not purely and entirely air-reduction processes, since the separation of the metal is also partially effected by means of charcoal or iron, or both of these agents, as will appear subsequently.

The *air-reduction processes* are particularly applicable to the treatment of rich ores, and such as contain a gangue of baryta, lime, and small quantities of blende; but not to silicious and refractory ores, which are better treated by the iron reduction methods of procedure. For the success of the air-reduction method, it is necessary that the ore (galena PbS) after sorting or picking, and washing, to free as much as possible from quartz and other silicious matters (operations conducted at the mine), be reduced to powder, and carefully roasted with access of air, the mass being continually rabbled, and the temperature properly regulated to prevent clotting of the ore; the effect of which treatment is to convert the plumbic sulphide largely into plumbic sulphate and oxide, according to the following equations, thus:



so that at the conclusion of this stage, there exists on the furnace hearth or bed, a mixture, in variable proportions, of plumbic oxide and sulphate, with unaltered plumbic sulphide; while upon increasing the temperature of the furnace, the plumbic sulphide reacts upon the plumbic oxide and sulphate, in both cases liberating sulphurous anhydride (SO_2), and separating metallic lead, as indicated in the following formulæ,



But since the roasting operations of the first stage can never be conducted with the precision necessary to ensure the presence of sulphur and oxygen in the mixture, in the exact proportions required to form sulphurous anhydride with one another, according to the last pair of equations; but either the sulphur or oxydized compounds, usually the latter, will be in excess, and accordingly remain behind, retaining a proportion of lead, which would be lost unless a special operation was conducted for its recovery; and it is the method pursued in the recovery of the metal from this residue that constitutes the chief difference in the conduct of the process and construction of the reverberatory furnaces employed in England, France, and *Carinthia*.

42. *Smelting in the Flintshire Furnace.*—The ore smelted in this furnace is a rich galena, assaying from 75 to 80 per cent. of metal, and occurring in a gangue of calcite, fluor-spar, and barytes. The ore, having been carefully separated by dressing operations from the gangue with which it was originally associated, is charged upon the concave bed of the furnace, immediately after the working off of a previous charge, and while the furnace is yet at a dull red heat; for its temperature has fallen considerably during the tapping out of the metal, and the withdrawal of the slag produced from the previous charge.

The *Flintshire furnace* is of the reverberatory type, having the fire-grate *a* at one extremity of the bed, from which it is separated by a hollow fire-bridge *b*, of from 18 to 24 inches in width, while the other extremity of the bed communicates by two openings or flues *g,g*, with a larger flue, which conveys the gases and lead fumes to a stack of some 60 ft. in height. The arched roof of the furnace is kept very low, and slopes from the fireplace to the flue end, and at a point near the middle of its length it is perforated by an aperture *c*, over which is suspended a hopper *d*, into which the charge is introduced, and then allowed to fall when required through the opening in the roof upon the bed of the furnace. The furnace is supplied with three doors *h,h*, upon each side. Through those at the front side the charge is rabbled, and the lime introduced as required towards the conclusion of the operation; while through those at the back

side of the furnace the slag is withdrawn after tapping out the metal. At the same time, the several doors serve for the admission of air at intervals during the first or roasting stage of the process; and likewise at the close of the operation the doors are opened to cool down the furnace previous to the

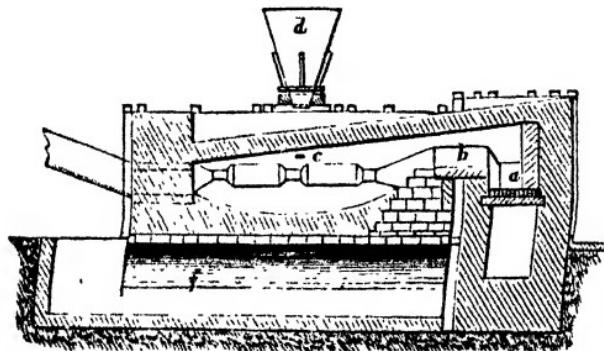


Fig. 15.—LONGITUDINAL SECTION OF THE FLINTSHIRE FURNACE.

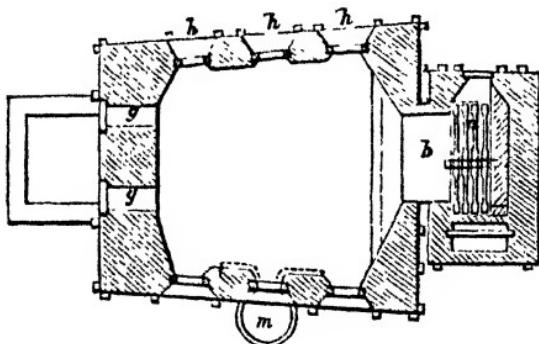


Fig. 16.—PLAN OF THE BED OF THE FLINTSHIRE FURNACE.

introduction of the succeeding charge, which object is further controlled by dampers placed in the flues at the end of the bed. Immediately below the middle door, on the front side, is placed the tap-hole for drawing off the metal from the well of the furnace into an iron pot *m*, placed outside for its reception, and known as the *lead-pot* or *lead-*

kettle. The fire-grate is only supplied with one door used for the introduction of fuel to the fire, and which opens to the back or labourer's side of the furnace; while over the ash-pit, in front of the fire-hole, is built a short flue for carrying away any vapours passing in that direction during the roasting. An arched vault, *f*, runs the full length of the bed, communicating with the atmosphere at both extremities; and upon this is built a course of brick-work known as the *cramp course*, upon which again is laid the brickwork forming a concave hearth, approximately of the form of the working bed, which slopes from the two ends towards the tap-hole, as also from the back towards the front; so that the metal, as it is reduced, collects in a kind of well over the tap-hole, at the *front or working side* of the furnace. But the working bottom of the furnace is formed of *grey slag*, the product of the working of the furnace itself; the slag being broken up and introduced into the red-hot furnace; where, after melting, the furnace is allowed to cool down again until the slag assumes a semi-fluid or pasty condition, in which state it is spread over the bricks by means of rakes, paddles, and bars, into a layer of from 6 to 12 in. in thickness, and of the form required to be given to the furnace bottom, after which it is left to solidify as the furnace cools. Such a furnace bottom requires about 5 tons of slag for its formation. The masonry of the furnace is braced together in the usual manner by stays and tie-rods; while, in some cases, the exterior of the furnace is formed wholly of iron plates, tied together by iron bolts or tie-rods.

The exact course pursued in the smelting of galena in this furnace, and the precise method of manipulation observed in the conduct of the process, differ in their detail as carried on at different lead-smelting establishments; as also at the same establishment upon a slight variation in the composition of the ore, especially with regard to the amount of quartz or of lime left associated with the galena; but generally the charge employed weighs about 21 cwts., besides a small amount allowed for draughtage to compensate for the moisture in the ore. This charge, as previously stated, is introduced from the hopper above the furnace, into which it is first delivered, on to the red-hot bed of the furnace; when

the first stage, or *calcination of the ore at a low temperature* commences; for which purpose the charge is kept upon the raised part of the hearth of the furnace above the well, the doors being left open for the admission of air, while the temperature is carefully regulated by the damper in the flue end, so as to raise the heat as high as possible, without fusing or clotting the ore; to prevent the latter, and, at the same time, to present fresh surfaces to the oxidizing influence of the air, the charge is kept continually stirred or rabbled. This (calcination) stage continues for from $1\frac{1}{2}$ hours to 2 hours, and at the end of this time the temperature of the furnace is raised by adding more fuel to the fire, and so exposing the charge to a higher calcining heat, care being taken that the temperature does not increase sufficiently to melt the charge. The effect of this calcination is to oxidize a portion of the plumbic sulphide to plumbic oxide and sulphate, according to equations (1) and (2) of page 94; so that in the next or *melting stage*, when the doors of the furnace are closed and the damper raised, whereby the temperature of the furnace is raised still higher in order to melt the charge, which then runs down into the well of the furnace, attended by a kind of ebullition from the escape of gases, due to a partial reduction of the lead by the reaction of the undecomposed plumbic sulphide with the oxidized products formed during calcination, according to the formulæ (3) and (4) of page 94. A few shovelfuls of slaked lime is now thrown into the furnace, in order to stiffen the mixture of slags and undecomposed ore, which is then raked on to the sloping sides of the bed, where it solidifies somewhat, and is then broken up and exposed during about an hour to a further calcination; upon the completion of which, the heat is again raised, and the charge melted down with the same decompositions as occurred in the previous *melting stage* of the process, and by which a further portion of metallic lead is separated. The operation of stiffening or *setting-up with lime*, followed by another calcination, is again repeated, but for a shorter period than before, after which the charge is again *melted down*, and the slags finally thickened or dried with lime, pushed back on to the higher parts of the bed, and the lead allowed to drain from them into the metallic

bath below. The furnace is now tapped into the lead kettle, and the slag, known as "*grey slag*," is withdrawn in pasty lumps through the back doors of the furnace.

A quantity of coal slack, along with a little live coals, are thrown upon the surface of the metal in the lead kettle, and are well mixed with the metal, by stirring the mixture with a perforated ladle; after which the metal is skimmed, and the skimmings containing sulphur, sulphides of lead, and iron, with small particles of unreduced ore, are returned to the furnace with the next charge.

The slags, as will subsequently appear, are rich in lead and oxidized compounds of lead. Since in the third stage, or setting up with lime and recalcination, it is the practice to produce a larger proportion of the oxidized compounds of lead than is necessary to react upon the undecomposed sulphide, hence an amount of lead escapes into the slag as oxide and sulphate, the former probably in combination with silica, derived from the materials of the furnace, etc.

The whole operation of working off a charge in this furnace occupies from 5 to 6 hours, with a consumption of about 12 cwt. of coal per ton of ore, and the production of about 5 cwt. of grey slag. The slag is the subject of a further treatment in the furnace known as the slag-hearth, for the more complete separation of its lead.

The action of lime in the above operation has been the subject of much speculation, and while it is asserted by some metallurgists, that its addition effects the decomposition of plumbic silicate and sulphate in the slag, yielding thereby plumbic oxide, calcic silicate, and calcic sulphate; yet these reactions appear doubtful, so that its chief use would rather appear to be to thicken or prevent the too great fusibility of the slags, permitting thereby of their better exposure for the oxidation of the plumbic sulphide in the calcination following the setting-up stage.

The grey slag is not always fused, the presence of foreign materials in the ores largely determining the fusibility or otherwise of the slag. Thus any zinc present in the ore, as blende, is not reduced during the smelting, but continues to accumulate in the slag at each stage of the process, and in which it is finally removed from the furnace, except such

proportion as may be volatilised during the smelting process; and the *alumina* also present in the ore accumulates in the slag as the reduction proceeds; while, as above stated, the slag also contains a large proportion of the oxidized compounds of lead, as is shown by the following analyses taken from Dr. Percy's work, Vol. III.

ANALYSES OF GREY SLAG FROM THE FLINTSHIRE FURNACE.

Plumbic Sulphide (PbS),	-	-	'90	...
Plumbic Sulphate (PbSO ₄),	-	9·85	13·269	
Plumbic Oxide (PbO),	-	48·87	24·375	
Zincic Oxide (ZnO),	-	7·52	22·857	
Lime,	-	12·68	11·190	
Alumina,	-	3·01	traces.	
Ferrous Sulphate and Oxide,	-	...	10·780	
Ferric Oxide,	-	2·86	...	
Combined Silica,	-	12·52	...	
Plumbic Silicate,	-	...	12·373	
Insoluble Residue,	-	1·43	...	
Carbon,	-	...	4·821	
Silver	-	...	'015	
		99·66	99·680	

The method of lead-smelting in the Flintshire furnace, as above described, thus comprehends four distinct operations:—

1°. Calcination of the charge at a low red heat, whereby a certain amount of plumbic oxide and sulphate are produced.

2°. Raising the temperature so as to melt the calcined products, thereby effecting a reaction between the above oxidized compounds and the unchanged ore, whereby a large proportion of the lead is reduced.

3°. Setting-up with lime, and the reduction of any residual sulphide; together with the formation of a larger proportion of oxidized compounds of lead than is required to effect the reduction of the plumbic sulphide.

4°. Tapping out the reduced lead, and subsequent withdrawal of the pasty lumps of grey slag.

43. Smelting Galena in Derbyshire, etc.—The galena obtained in this district is usually associated with plumbic carbonate (cerusite), and baric sulphate (heavy-spar), of which the latter, from its great specific gravity, is not easily separated from the galena by the ordinary mechanical opera-

tions of washing, so that in smelting the ore it is necessary, if *fluor-spar* is not a constituent of the gangue of the ore, to add this mineral, with about one-fourth of its weight of *calc-spar*, in order to flux or separate by fusion the barytes; and thus, instead of obtaining grey slag as produced at Holywell, in Flintshire, the Derbyshire furnaces yield a compact, opaque, yellowish, or brownish slag, which is tapped out of the furnace, and is known then as "*run slag*," while there remains in the furnace a small quantity of a heterogeneous, porous, and greyish-looking mass of slag, more infusible than the run slag, and which is drawn out from the furnace as at Holywell, in the manner already described, and which second slag is hence known as "*drawn slag*." The furnace employed in this district is a reverberatory furnace, very similar to the Flintshire furnace described in the last Art., except that since a portion of the slag is fused, two tap-holes are provided, from one of which the metal is tapped, while the slag is run out from the second; and the furnaces are generally somewhat smaller than those employed in Flintshire, since the charge is about 25 per cent. less in weight; but the manipulation observed is much the same in the two cases, *lime* being employed as before in *setting-up*, but the *run slag* is run from its tap-hole previous to the tapping of the metal into the lead kettle; while in the Flintshire process, the metal is first tapped out, and the slag afterwards raked out through the door at the back side of the furnace.

44. Lead Smelting in the Brittany Furnace.—A variety of the Flintshire reverberatory furnace, but with three doors along the front side only, is known as the "*Brittany furnace*," from its former use in the province of Bretagne for the smelting of a galena, containing from 12 to 18 per cent. of iron pyrites. These furnaces are usually built of large blocks of granite held together by tie-rods. The Brittany furnace, though generally of smaller dimensions, yet otherwise resembles the Flintshire furnace; for the hearth slopes from both ends, and from the back of the furnace towards the front side, while the lead kettle is situated as before under the tapping hole in front of the middle door; but the charge is introduced on to the hearth through the side doors, instead

of through the roof; and the manipulation pursued in the smelting of galena with this furnace differs somewhat from that observed when smelting it in the Flintshire furnace, inasmuch as the temperature employed in the Brittany is generally lower than in the Flintshire furnaces, and the metal is tapped off several times during the smelting operation.

The course adopted in Bretagne consists in gradually heating the charge upon the furnace hearth until it begins to soften, upon which it is vigorously rabbled, when a quantity of metal separates by the reaction of plumbic oxide and sulphate with plumbic sulphide, according to the reaction already formulated; and the metal so reduced is drawn off into the lead kettle outside the furnace. This rabbling is succeeded by a second period of calcination, lasting about two hours, when the mass is again vigorously rabbled or stirred, with the reduction of a further quantity of metal as before, which is again tapped from the furnace; and these calcinations, each one conducted at a higher temperature than that previously employed, and followed by stirring, are continued for about 13 hours, the reduced metal having been run out after each rabbling of the mass; and at the end of this period, an excess of oxidized compounds of lead exists in the charge, for the reduction of which a quantity of wood and coal-slack is thrown into the furnace, when after the separated metal has again been tapped off, the charge is subjected to a last roasting and stirring before the grey slag is withdrawn from the furnace. The grey slag still retains from 35 to 40 per cent. of lead, chiefly as plumbic sulphate and silicate; and after the treatment of the slags in the cupola furnace, the total yield of metal by the Bretagne process yet falls short of that obtained in England in the Flintshire furnace.

The lead is generally purified by stirring or *poling* with wood; the skimmings so produced, and which contain sulphides of lead and iron, with sulphur and particles of the unreduced ore, being removed as they collect at the surface of the metal. But copper, antimony, and arsenic cannot be removed by this treatment; and for their removal, when present, it is necessary to refine the lead in the manner described in page 155.

45. Lead Smelting in Spain.—The ores occurring in Spain are galenas, containing an average of from 75 to 80 per cent. of lead; and the method of smelting them is similar to that described in the previous articles, except that smaller charges are used, and instead of "setting-up" with lime after the melting down, it is usual to apply charcoal for this purpose. But an essential difference exists between the Flintshire furnace and the Spanish furnace or *Boliche*, inasmuch as the Boliche is a reverberatory furnace having two arched chambers or hearths, separated from each other by a bridge or partition, in which are two flues or apertures of communication between the one and the other; while from the second chamber passes a single flue to a stack of about 30 ft. in height. The first or *reduction chamber* communicates, at the end furthest from the stack, with a fireplace fed from one side of the furnace with brushwood or similar fuel occurring in the neighbourhood, for the combustion of which class of fuels the furnace appears to be well adapted; and the bed of this chamber slopes from the back or flue end towards the front, where it forms a cavity or well in which the metal collects, and from whence it drains into a circular vessel or receptacle outside, from which it is tapped into a channel communicating with a reservoir, and from thence, after the mechanical impurities have been removed by stirring dried leaves, etc. (instead of the coal or wood used in the Flintshire process) with the lead, whereby the dirt, etc., rises to the surface of the metal as a scum, which is taken off; the metal is cast into ingots.

The reduction chamber is only provided with one door, situated at the front of the furnace, and through which the charge of ore is introduced by large two-handled scoops; while the same door also serves as the working door of the furnace, and for the rabbling of the charge. The second chamber of the furnace, situated between the last one and the stack, is very wide but short; it has no openings except the flues, which are placed at opposite sides of its shortest dimension, and communicate with the reduction chamber and the stack respectively, while its use does not appear to be clearly understood, but it is said to regulate or control, in some manner, the draught of the furnace.

The method of procedure in smelting galena in the above furnace is very analogous to that already described, the charge of ore being spread evenly over the bed of the furnace, and calcined, during about an hour and a half, with frequent rabbling of the charge during the operation. The charge is then melted down, and the residue is *set up* with small charcoal and again roasted; so that, during the second calcination, the plumbic sulphate and oxide produced in the first calcination, and remaining undecomposed after the first melting down, may be partially reduced by the charcoal to plumbic sulphide and metallic lead respectively; while the plumbic sulphide so produced is ready to react in the next fusion upon any undecomposed plumbic sulphate and oxide in the manner indicated on page 94, with the separation of metallic lead. After the metal is tapped out, there remains a *grey slag*, analogous to that occurring in the Flintshire furnace, and this is smelted in a blast furnace for the recovery of its lead.

46. Bleiberg or Carinthian Process —A method known by these names, and analogous to that described in the last article, is pursued in the neighbourhood of Bleiberg, in the province of Carinthia, in Austria, where it is employed for the smelting of a comparatively pure, but practically non-argentiferous galena. The process involves three stages—
1°. *Roasting or calcination* of the ore at a gradually increasing temperature, for the production of plumbic oxide and sulphate. 2°. *The liberation of metallic lead*, due to an increase in the temperature of the furnace, accompanied by vigorous rabbling, whereby the unaltered plumbic sulphide reacts upon the oxidized products of lead in the manner already described. 3°. *Reduction by carbonaceous matters* of the oxidized compounds of lead present in the slag produced in the last stage.

When pure ores, that is, such as do not contain much silica, although small quantities of lime, baric sulphate (heavy spar), and zinc blende may be present, are operated upon by this method, it affords a purer and softer lead than other methods, with a good yield of metal, and with the production of only a small quantity of slag, which is, moreover, poor in lead; but for these results the process entails a large con-

sumption of fuel, with a considerable expenditure of time and labour.

The construction of the Bleiberg reverberatory furnace differs materially from any of the preceding. It consists of a chamber *a*, measuring about 10 ft. 3 in. from back to front, and about 4 ft. in width at the back; while from the middle to the front or *working door b*, it gradually narrows as shown. The *fireplace d* is a long narrow chamber along one side of the furnace, the back of which, however, only receives the fuel, and communicates with the atmosphere from beneath; so that the flame passes over the fire-bridge *m*, along the surface of the bed or hearth of the furnace, and escapes by a flue situated immediately over the working door to a chimney *c*, about 27 ft. in height, and which serves for a pair of furnaces, usually built together. The bed of the furnace is formed by first ramming upon the brickwork a layer of clay, of about 6 in. in thickness and shaped to the form of the bed, while upon this rests the working bottom, formed of lead slags of about the same thickness. The finished hearth is hollow or concave from side to side, and slopes gradually from back to front, or from the fire-bridge to the flue as shown in fig. 18, so that the melted materials from all parts of the furnace drain down to the lowest point at the front end of the bed, where the tap-hole is placed, and from which the metal flows from the furnace into a trough *n* placed outside. In front of the working door is a flue *p*, which communicates with the main flue leading to the stack, and which serves to carry off to the latter any deleterious fumes escaping from the working door. The fuel employed in this furnace is generally spruce and pine woods; but by a little alteration in

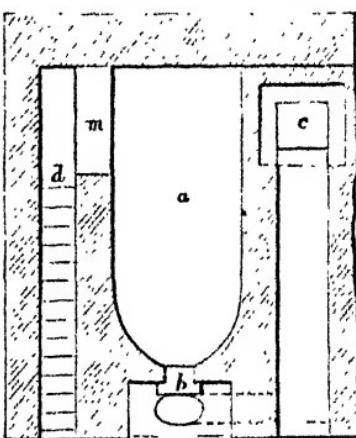


Fig. 17.—PLAN OF THE BED OF THE BLEIBERG FURNACE.

construction, it permits of the substitution of brown coal in lieu of the wood.

The charge of from 3 to 4 cwt.s. of ore is introduced on to the hearth through the door *b* at the front of the furnace, and is spread uniformly over the surface of the hearth,

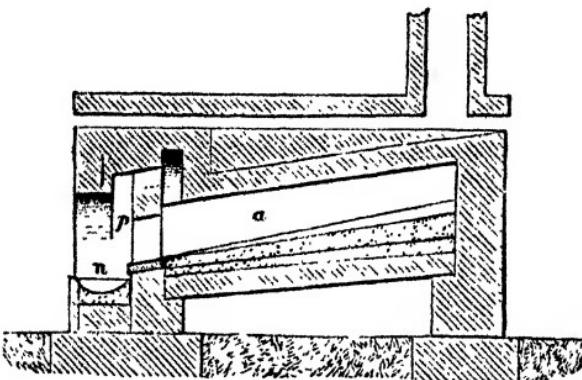


Fig. 18.—LONGITUDINAL VERTICAL SECTION OF THE BLEIBERG FURNACE.

where it is exposed to calcination at a low temperature during from 3 to 3½ hours; and during this stage the mass is frequently rabbled, while at its conclusion the temperature is raised, and the charge again rabbled vigorously, when mutual decomposition of the plumbic oxide and sulphate with plumbic sulphide ensues, constituting the second stage of the operation, during which the separated lead runs from the tap-hole into the cast-iron pot placed outside for its reception ; and when lead ceases to flow, the residue or slag remaining upon the hearth of the furnace is either thickened by the addition of the ashes and small charcoal from the ash-pit, and then drawn from the furnace until another charge has been worked off, when the slag from the two charges is treated together, or, instead of thus withdrawing the first charge, while a second is worked off, the slag may be at once *treated with charcoal*, constituting the third stage of the process, in which case the mixture of slag and small charcoal is thoroughly rabbled, and the temperature raised considerably with the maintenance of a reducing

atmosphere in the furnace, whereby the plumbic oxide and sulphate of the slag suffer reduction by the carbonaceous matters, yielding thereby about 20 per cent. of metallic lead. The whole operation of working off two charges of ore in this manner, with the separation of metal from the slag produced by the first operation, occupies from 21 to 23 hours.

47. Cornish Process of Lead Smelting.—In Cornwall and certain Continental works, an impure galena, yielding from 60 to 70 per cent. of lead, and associated with *quartz* and *fluor-spar*, with sometimes also *zinc blende*, *spathic iron ore*, *fahlerz*, etc., is smelted in two stages, conducted in two distinct reverberatory furnaces, known as the "*calciner*" and the "*flowing furnace*" respectively, of which the former is of larger dimensions than the latter.

The reduction of the metal is effected according to the method here pursued, partly by the reaction of the oxidized products of lead resulting from the calcination of the charge, upon the unaltered sulphide, as in the Flintshire furnace; but a further decomposition is effected in this process by adding to the charge of the flowing furnace about 5 per cent. of pieces of *scrap-iron* along with a quantity of *culm* (small anthracite), both of which liberate lead from the ore; so that instead of metal and slag alone being produced as in the previously described processes, there is, according to this treatment, *metallic lead*, which is first tapped out from the furnace; above which is a *regulus* from which a further quantity of lead can be separated by a subsequent smelting; while lastly, a *fluid slag*, practically free from lead, and known as *run slag*, is tapped from the furnace; and, further, when smelting the argentiferous ores imported from South America according to this process, then a fourth product or *speise* is obtained, so that *lead*, *speise*, *regulus*, and *slag* are successively tapped from the furnace. The Cornish method thus forms a connecting link between the air-reduction process, as pursued in the Flintshire furnace, and the "iron-reduction" process, as conducted in the blast and cupola furnaces to be hereafter treated upon; and as already noted, "anthracite" is also added to the charge, so that the method of smelting lead in the flowing furnace affords an example of a combination of the methods tabulated on p. 93.

The Cornish method of reduction is also pursued in North Wales, etc., for the separation of the lead from the rich grey slags produced in the Flintshire furnace, as also for the treatment of various other lead residues. The lead obtained by this process is however generally hard, and requires softening before being ready for use, while any copper present in the ore passes into the regulus, or *slurry*, as it is called.

The *calcining stage* of the Cornish process is effected in a reverberatory furnace, in the roof of which is an opening for the introduction of the charge, previously dried by exposure upon the top of the calciner. This furnace has a door at each side, and one at the flue end of the bed; the fire-bridge is built hollow, and beneath the bed of the furnace is a vault or cave, into which, at the close of the calcination, the roasted materials are raked through two openings in the furnace bottom, situate one at each side of the furnace, beneath the back and front doors respectively. The ore for calcination, having been dried on the top of the furnace, is introduced through the opening in the roof, and spread over the bed of the furnace, where it is exposed to the heat and oxidizing atmosphere of the furnace for from fifteen to twenty hours, during which time the charge is frequently rabbled, and a little lime thrown in as occasion requires, to prevent clotting of the ore; and at the end of the calcination the charge is raked through the opening already mentioned into the vault below, when a fresh charge of ore is introduced through the roof on to the bed of the furnace. The charge of these calciners varies from 25 to 60 ewt. of ore, according to the size of the furnace.

The calcined or roasted ore is introduced into the "*melting*" or "*flowing furnace*" through the two doors at the back side of the furnace, and is spread over the hearth or bed, when the furnace doors are closed and the heat raised, whereby the charge of about two tons is melted down in from two to three hours, attended with the separation of a certain proportion of lead reduced by the reaction of plumbic sulphide upon the oxidized products—plumbic oxide and sulphate—produced during the previous calcination, exactly in the manner described with the Flintshire furnace; and if the ore be rich, the proportion of lead so separated will be con-

siderable, and is at once tapped out. The melted charge is next *dried* or mixed with a quantity of *lime* or *culm* (powdered anthracite), and again spread over the bed of the furnace, when from 1 cwt. to 2 cwt. of *scrap-iron* is introduced, upon which the doors are again closed and the charge remelted, by which the iron and carbonaceous matters act upon the plumbic compounds, with the separation of metallic lead; while a portion of the iron, combining with sulphur, yields ferrous sulphide, which, in combination with other sulphides present in the ore, form a *regulus* or *matt*; so that on again tapping the furnace, lead, regulus, and slag run successively from the tap-hole into the lead pot placed outside the furnace beneath the tap-hole, the slag being allowed to overflow the pot into a gutter which conveys it to a pit arranged for its reception. The iron probably also decomposes *plumbic silicate*, formed during the fusion of the lead compounds (notably of plumbic sulphate), with the quartzose gangue with which the ore is associated, yielding thereby a slag of ferrous silicate and liberating metallic lead.

The *flowing furnace* employed in the fusion differs but slightly from the Flintshire furnace already described, the latter has, however, six doors, while the flowing furnace has only four, viz., two upon each side of the hearth, while the working bottom is in both cases formed of lead slags, and in the flowing furnace it is concave, sloping from both the fire-bridge and flue-end towards the middle, while it slopes also from the back towards the tap-hole. The hearth measures about 14 feet in length and 8 feet in breadth.

The working off of a charge in the flowing furnace usually occupies about eight hours, from the time of charging the furnace to the final tapping out of the slag; and the slags are usually sufficiently clean to admit of being thrown away, since they do not yield more than 1 per cent. of lead.

48. Smelting in the Ore Hearth.—In the north of England, especially in the counties of Durham, Cumberland, Northumberland, and Yorkshire, it is the practice to smelt lead ores, or, as it is here called, "*bouse*" in the furnace (fig. 19), known as the *ore hearth* or *Scotch furnace*, and which consists of a rectangular chamber or cavity (*a*) of some 24 inches in length, 12 inches in breadth, and from 22 to 26 inches in depth,

which is lined entirely with cast-iron plates, the bottom being formed of one piece. The cavity or hearth is enclosed by a kind of arched hood (*b*) for carrying away the fumes, etc., produced during the smelting; while through the back of the furnace, and resting upon the *back-stone* (to be presently described), is introduced a twyer, through which a blast of air can be maintained. At the front end of the cavity or hearth (*a*) is placed the *work stone* (*c*), surrounded by a ledge on all edges except that nearest the hearth; while from top to bottom of this plate is cut a groove, gutter, or channel, along which the lead flows into the lead pot outside as the hearth fills and

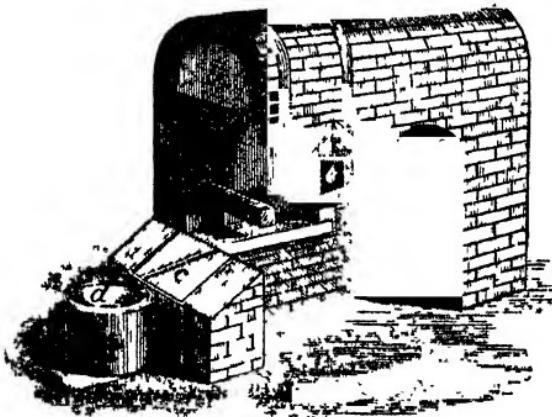


Fig. 19 ELEVATION OF THE OFF HEARTH, PARTLY IN SECTION.
overflows with metal. The work stone inclines from the hearth (*a*) to the *lead pot* (*d*), and its top edge is about 5 inches above the bottom of the hearth. At the back of the furnace is placed the cast iron prism or *back-stone* (*e*), upon which is placed a similar cast iron prism (*f*), known as the *pipe-stone*, and which projects a short distance over the cavity of the hearth; while surmounting the pipe-stone is another cast-iron block, known as the *upper back-stone*, and along the sides of the furnace, resting upon the hearth bottom, are placed two prismatic castings or *bearers* (*g*), on which rest the extremities of the front prism of cast-iron analogous to the back stone, but which is known as the *fore-stone*, each extremity of which is

received between two cast-iron blocks placed upon the bearers of each side, and known as *key-stones*—by moving which backwards or forwards the fore-stone can be moved in the same direction. At the sides of the furnace, on the level of the key-stones, is an opening through the brickwork, through which the workmen clear away any slag adhering to the twyer, and also introduces a peat before the nozzle in commencing and during the working of the furnace.

The several parts of this hearth are described as *stones*, although each is made of cast-iron; and the hearth, as described above, is supported by brickwork, or brickwork and rammed clay, as shown in the figures.

The ore or *bouse* for smelting in the ore furnace is at certain works first calcined in a reverberatory furnace, in charges of about half a ton at a time, the roasting being continued at a moderate temperature during about eight hours, while the heat is increased towards the close, so as to slightly agglutinate the ore, and so prevent the finer particles from being carried into the flue by the mechanical action of the blast in the ore hearth. During the roasting the mass is frequently rabbled or stirred, the sulphur with antimony (if present) being oxidized, and partially escape as sulphurous anhydride and antimonious oxide respectively; while plumbic sulphate and oxide are produced at the same time, and remain in the bouse to be charged into the ore furnace. The ore is then raked from the furnace or calciner, and, if necessary, thrown into a pit of water, or water is thrown over the heated mass, so as to break it up ready for charging into the ore hearth. At other works the ore is *not* calcined previous to smelting, but is charged directly into the ore furnace for reduction.

Supposing the ore furnace to be cleaned out from a previous operation, the rectangular cavity or chamber (*a*) is filled with *peat*, judiciously arranged around the hearth, since peat, with only a small proportion of coal, constitutes the fuel of this furnace, which affords accordingly the only example of a metallurgical process in use in England where peat is the fuel employed. The peats being properly arranged in the hearth, an ignited peat is then placed in front of the twyer, and the blast is turned on, whereby combustion rapidly spreads

throughout the furnace, upon which a little coal is added, and shortly afterwards a small portion of the partially reduced ore mixed with slag and cinders, which remains upon the hearth at the end of each shift, and which is technically known as "*brouse*" or "*brouse*," is thrown into the hearth, when, after the lapse of about half an hour, the temperature having in the meantime increased, and lead began to flow from the brouse, the contents of the hearth are stirred up and a portion of the charge is thrown forward on to the *work-stone* (*c*), and any *grey slag* is separated, when the residue is returned to the furnace and the regular working of the hearth succeeds; the charge being thus worked upon a bath of metal contained in the bottom of the hearth, and upon which the ore and fuel float. But the working requires a careful manipulation of the peats which are judiciously placed before the twyer, so as to distribute the blast uniformly over the hearth, while the ore or bouse is added to the furnace charge in small quantities at a time, always introducing it on to that part of the hearth which appears hottest, when the work then proceeds regularly, with the introduction of peat-fuel and bouse as required, the workmen stirring the charge with iron bars at intervals of about five minutes; whilst at intervals of about twenty minutes they throw forward a portion of the charge on to the *work-stone* for the separation, as before, of grey slag, and to permit of the breaking up of any large lumps of brouse that may have collected; after which the *brouse*, with a certain quantity of coal and quick lime, is returned to the furnace, and a fresh supply of raw or roasted ore is placed on the top, while, at the same time, another workman introduces his bar into the furnace and detaches any slag, etc., that may have attached itself to the twyer. Lead is now freely reduced from the ore, and collects in the bottom of the hearth, which it soon overflows, and passes along the gutter or channel in the middle of the *work-stone* into the kettle or lead pot (*d*), which, when full, is skimmed, and the metal ladled out into moulds forming pig-lead. In a shift of from twelve hours to fourteen hours the above furnace will yield about 2·5 tons of lead.

The method of manipulation, detailed above, is somewhat modified in different works—thus, after separating the grey

slag on the work-stone, and breaking up any lumps of browse, it is the practice in some works (only if the latter shows a tendency to become pasty) to spread over it, before returning to the furnace, a little slaked lime in powder, and thereby prevent its clotting.

The temperature employed in the ore furnace or Scotch hearth is much lower than that employed in the Flintshire and other reverberatory furnaces hitherto described, and the reduction of the ore is effected largely according to the reactions (already described, p. 94) between plumbic oxide and sulphate with plumbic sulphide—the formation of oxidized products for effecting these decompositions being promoted by the exposure to the action of the atmosphere of the heated browse upon the work-stone, in the manner described; while possibly a smaller proportion of metal may also be reduced by the action of carbonaceous matters upon the oxidized compounds of lead.

The slag obtained in this process, though not very large in amount, is rich in lead, existing partly as metallic particles mechanically diffused throughout the slag, and also as plumbic oxide, sulphate, silicate, and undecomposed sulphide—the total amount of lead so retained being found in a specimen of slag to amount to 31 per cent.* of the slag; while the slags generally retain on an average about 10 per cent. of the total amount of the lead in the ore. Other constituents of the slag are lime, magnesia, zincic oxide, ferrous oxide, alumina, silica, baric sulphate, mechanically mixed carbon, etc.,—the whole constituting a very heterogeneous mass of materials.

The ore furnace cannot be worked uninterruptedly, since it becomes too hot.† To overcome which difficulty it has been proposed, as in the American hearth, to make the hearth-box hollow, and so cool it by blowing air around the hearth.

The ore furnace is applicable to the treatment of poor ores in districts where peat is abundant, and coal more or less scarce; but where coal is cheap and abundant, this furnace cannot be applied to the smelting of lead in opposition to the reverberatory furnace.

49. The American Ore Hearth.—This modification of the ore furnace or Scotch hearth, last described, was formerly in

* Percy. *Metallurgy*, Vol. III. † *Ibid.*

use in the United States, Carinthia, Bohemia, etc. It is arranged so as to heat the blast of air employed in the furnace, effecting thereby an economy in the amount of fuel required, while, at the same time, the circulation of the blast is made of service in keeping down the temperature of the hearth.

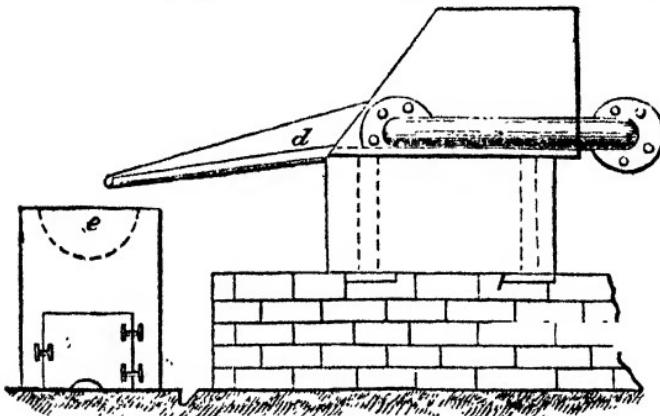


Fig. 20.—ELEVATION OF THE AMERICAN ORE HEARTH.

With these objects, the cast-iron walls of the hearth are made hollow, and the blast which is introduced by the pipe (*a*) is made to circulate in the direction indicated by the arrows (fig. 21) around the hearth before entering the furnace by the twyer at *b*. The lead, as it is reduced, collects in the hearth (*c*), as in the last furnace, and, overflowing the hearth, flows along a channel in the work-stone (*d*) to the receiver (*e*).

Wood is the fuel employed in this furnace, and the method pursued in its working is but a modification of that last described. The hearth (*c*) being filled with metal, and the charge worked upon this bath in the manner described in the last article, except that instead of peats, the workman introduces pieces of wood before the twyer for distributing the blast etc., and charges the furnace with raw ore (galena); when the smelting is attended with the same cycle of oxidizing and reducing reactions as before, care being taken, however, that the temperature of the furnace be not sufficiently intense to fuse the galena, otherwise the reduction of metal is much checked, and hence also the desirability of using a light fuel,

as wood, in lieu of the more dense combustibles which would afford too great an intensity of heat. The blast is shut off while the charge is brought forward on to the work-stone; and the charge is reintroduced into the hearth after the necessary breaking up, etc., along with a fresh quota of ore, before the blast is again turned on—the amount of blast introduced being controlled by a suitable valve opened and closed by the workmen as required.

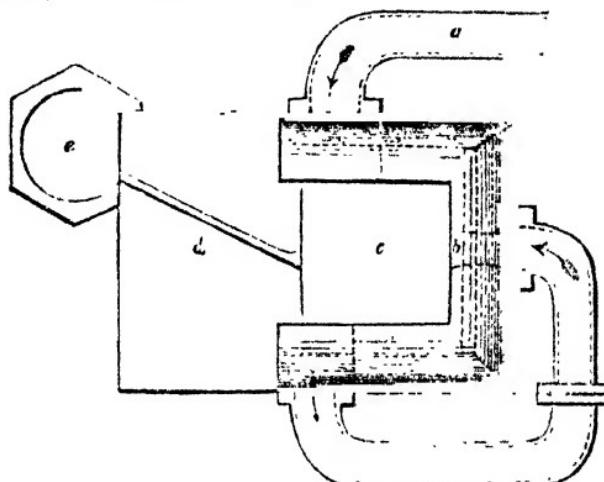


Fig. 21.—PLAN OF THE BED OF THE AMERICAN ORE HEARTH.

The following is given by Plattner as the composition of the slag produced in the American ore hearth at Bleiberg, in Carinthia :—

Silica,	-	-	-	-	-	5·260
Sulphuric Acid,	-	-	-	-	-	5·038
Plumbous Oxide,	-	-	-	-	-	37·710
Ferric Oxide,	-	-	-	-	-	19·500
Zincic Oxide,	-	-	-	-	-	19·200
Molybdic Acid,	-	-	-	-	-	·460
Lime,	-	-	-	-	-	8·856
Magnesia and Manganese Oxide,	-	-	-	-	-	1·417
Alumina, with traces of Potash, Soda, and					1·760	
Cuprous Oxide,	-	-	-	-	-	

IRON-REDUCTION PROCESSES FOR THE SMELTING OF LEAD ORES.

The methods of reduction by *iron*, or by *iron-yielding materials*, as iron ores, iron scales, basic ferrous silicates, etc., which afford iron by contact with carbonaceous matters in the furnace, are employed in Silesia, Saxony, Bohemia, the Hartz, Japan, etc., for the reduction of lead from galena, or from oxidized products, as plumbic silicates, etc., as well as for the treatment of the less pure, quartzose, argillaceous, or more refractory ores and products. Such as ores containing, in addition to lead, a considerable percentage of zinc, copper, antimony, etc., or more than about 4 per cent. of silica, which ores do not readily yield to the air-reduction processes, owing to the formation of plumbic silicate, which impedes the reduction in the reverberatory furnace, and gives rise to residues which are rich in lead; such ores, then, are best treated with iron in the blast furnace, since, as already stated (pp. 81, 82, and 85), both the sulphur and oxy-compounds of lead are completely reduced when heated with metallic iron. Both the blast and reverberatory type of furnace have been employed in the reduction of lead by means of iron, but the blast or cupola furnace is more economical, and of more general application in these methods. The blast or cupola furnace generally employed is of small dimensions, ranging from 3 to 5 feet in diameter, and only from 10 to 20 feet in height.

The method of lead smelting, as conducted in the "flowing furnace," already described, forms a transitional stage between the "iron-reduction" processes, as pursued largely upon the Continent, and the "air-reduction" process generally employed in England.

Two types of procedure are observed in the treatment of lead ores, by the methods of reduction by iron, according to which the *raw ore* is either treated directly with iron or ferriferous matters, or the ore is first *roasted* and then treated in the blast furnace with *iron* or iron-bearing materials; the latter method being generally applied to such ores as contain large proportions of earthy and metalliferous impurities, and to the treatment of lead regulus. But in either case three products are obtained as the result of the smelting operation, viz.:

1° *Lead*, which is generally sufficiently argentiferous to be directly treated by cupellation, for the extraction of its silver; 2°, a *regulus* or *matt*, consisting chiefly of ferrous and plumbic sulphides, but retaining also a proportion of silver, and which matt is again treated in a subsequent operation; and 3°, a *slag*, containing variable proportions of lead, according to which it is either thrown away, or again smelted for the recovery of its metal.

50. Lead Smelting in Silesia — At Tarnowitz, etc., in Upper Silesia, the method of smelting silicious lead ores in blast furnaces, employing *iron* as the reducing agent, with charcoal, coke, or coal as the fuel, has been employed. But *coke* is generally preferred as yielding a *regulus* which is poorer in lead than when charcoal is employed, while affording a greater yield of metal, with a shorter duration of the smelting operation than when coal is used as the fuel; but with the introduction of more perfect blowing apparatus coal has been adopted. The furnace employed (fig. 22), and resembling the slag-hearth described in pp. 136, 137, is formed of an inner lining (*a*) of fire-brick enclosed in an outer wall of common brick; the furnace is supplied with one inclined twyer (*b*), situated at the back of the furnace, and at about 15 inches above the level of the fore-hearth. The hearth and shaft (*c*) are rectangular in section to the height *d*, where it becomes

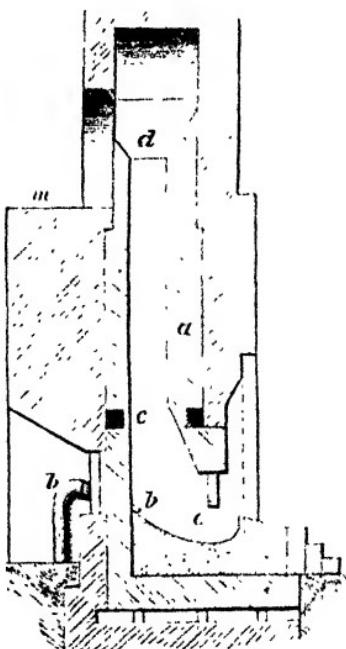


Fig. 22.—VERTICAL SECTION OF THE BLAST FURNACE EMPLOYED IN UPPER SILESIA FOR THE SMELTING OF LEAD. (Joachimsthal).

circular, and communicates with a series of chambers for the condensation and collection of any fumes that may be volatilised, or of arresting particles mechanically carried by the blast from the furnace hearth. The hearth (*e*) is composed of a brasque of equal parts of clay and coke dust, and communicates with the fore-hearth by an opening or eye, through which the slags are drawn off; while a communication is made with the bottom of the hearth, for tapping out the metal and regulus into separate receptacles placed in front, the tap-hole being closed by a plug of clay, except when drawing off the metal.

The mixture of ore, fuel, flux, etc., is introduced from a platform *m*, through an opening near the top of the furnace shaft; the charge consisting of about 100 parts of raw ore, with 12 to 15 parts of *cast* or *scrap iron*, from 12 to 14 parts of *iron slugs* or forge scales, and about 30 parts of lead slags; a charge of these proportions requiring for smelting about a ton of coal per ton of ore.

The furnace is charged or fed by throwing the ore mixture against the back side of the furnace, while the fuel is introduced towards the front; the effect of the distribution of the materials in this manner being to form a *slag-prolongation* or *nose* upon the end of the twyer, and which prolongation, according to its length, affords a dark or bright *eye* or opening at its end, by which the workman is enabled to observe the working, and adjust the charges to the requirements of the furnace; thus, if the temperature falls, the *nose* becomes longer and more nearly closed at the end, the "eye" becoming accordingly less luminous, indicating thereby that the *burthen is too heavy*, i.e., that there is an excess of ore to fuel in the furnace charge; while on the other hand an excess of fuel in the charge burns away or melts the nose, affording a brighter "eye," and causes the temperature near the front wall to be lowered, owing to imperfect distribution of the blast by the shorter nose, whereby slag, etc., adheres to and forms accretions on the front wall impeding the proper descent of the charge.

As above stated, the products of smelting in this furnace are a *rich lead*, which is at once treated for the extraction of

its silver; secondly, a *regulus* of ferrous sulphide produced by the reaction of the iron upon the plumbic sulphide in the separation of metallic lead, and which regulus also contains more or less undecomposed plumbic sulphide with a little silver, along with smaller and variable proportions of other metallic sulphides, such as those of copper, zinc, antimony, nickel, manganese, etc.; this regulus being treated for the extraction of its lead and silver by roasting and subsequent treatment as a roasted ore in the blast furnace; while lastly, there results a proportion of *slag*, containing variable amounts of lead, and which is classed as *clean slag*, if containing only about 2 per cent. of lead, and is then thrown away; or, if it retains upwards of 6 per cent. of metal, the slag is called *unclean*, and is again smelted, either alone or as part of a subsequent furnace charge, serving thereby to give the required fusibility in the treatment of the richer ores of the district.

The *low blast furnace*, described above, was employed in the smelting of such rich ores as occur in fragments, and contain from 75 to 80 per cent. of lead, while the poorer ores, and the *schlech* or *slices* from the first-mentioned ores, were smelted in the high blast furnace; but the method of smelting in the blast furnace has been largely superseded at Tarnewitz by the method of reduction in the reverberatory furnace. The Silesian low blast furnaces work continuously during eight or ten days, when it is found necessary to stop the smelting, in order to repair the interior of the furnace.

51. Lead Smelting in the Hartz.—The method of smelting here pursued is applicable alike to the treatment of ores containing considerable proportions of foreign sulphides, or to the smelting of lead regulus. The method comprises two stages, the first, or *roasting*, is usually performed in the district of the Hartz in pyramidal heaps, containing from 75 to 150 tons of ore or regulus, while in other districts adopting this method of smelting, the reverberatory furnace is applied to the purposes of roasting the ore. In the second stage, or *fusion*, the roasted materials are smelted in admixture with silica, slags, and residua from the various operations in the smelting and cupellation of lead, along with *scrap-iron* or granulated *cast-iron*; but the addition of metallic iron is not

now universal, for if the roasting be conducted with considerable care and attention, the necessity of adding iron is avoided, and its use has been accordingly discontinued at some of the works; and the method has been generally superseded by the method of smelting in the Rachette furnace, employing basic ferrous silicate (finery slags or highly ferruginous copper slags) as the reducing agent, as will be described in the next article. The fusion is effected in the Hartz district in low blast furnaces, employing either coal, coke, or charcoal as fuel.

The *roasting of the ore or regulus* is usually conducted in the district of the Upper Hartz as at Rammelsberg, etc., in pyramidal heaps; for which purpose a layer of pine wood is first placed upon a level and solid piece of ground, and this is succeeded by layers of the ore, broken into pieces of about the size of the fist, the smaller pieces being placed in the layers near the top of the pile; while above this, and completing the pile, is applied a layer of small ore or regulus which has been previously once roasted, whereby a too rapid combustion of the sulphur in the ore is prevented. The heap is fired by igniting the wood in the bottom of the pile, when the combustion is chiefly continued by the oxidation of the sulphur in the ore, a portion of which is sometimes collected in the top of the pile by forming a series of cup-like depressions in the upper surface of the covering of the pile, whereby a portion of the sublimed sulphur collects in these cavities, and is ladled out from time to time. The first firing continues for from two to four weeks,* when the pile is broken up and the brownish-grey earthy-looking lumps of well roasted ore are separated from the raw or imperfectly roasted portions, the operations of roasting and separating being repeated again and again upon the same charge of ore for some six or eight times in succession, and each time with the addition of a fresh quantity of wood and rearrangement of the pile, so that the more imperfectly roasted pieces are each time put towards the base of the pile, and thus subjected to the greatest heat; the total period of roasting thus occupies from fifteen to twenty weeks for its completion, each firing being of shorter duration than its predecessor.

* Kerl. *Handbuch der Metallurgischen Hüttenkunde.*

The ore or regulus before roasting consists largely of the sulphides of lead, iron, copper, zinc, etc., of which the first mentioned is converted by the roasting into a mixture of *plumbous oxide* and *sulphate* (p. 80), the ferrous sulphide likewise by oxidation becoming ferrous sulphate, and eventually ferric oxide (p. 46, Vol. I.), while the sulphides of zinc and copper likewise are converted, as described on pages 14, 163, respectively, into their respective oxides.

The *smelting* or *fusion* of the roasted product is conducted in a low blast furnace, with the production thereby of—^{1°} An *argentiferous* and frequently *auriferous* lead. ^{2°} *Lead regulus*, consisting largely of the sulphides of lead and copper, with smaller quantities of ferrous sulphide, and still retaining also some silver. ^{3°} *Lead slags*, consisting of a basic silicate of iron, with alumina, cuprous and plumbic oxide in small quantities; while magnesia, lime, manganous oxide, zincic oxide, antimonious oxide, and sulphur are one or more frequently present in small quantities. The smelting mixture varies much in different works, but a charge employed at Rammelsberg consists of 35 cwt. of the roasted ore, 10 cwt. of silicious slags, together with from $\frac{1}{4}$ to $\frac{1}{2}$ cwt. of plumbiferous residues, which ingredients are mixed on a floor just below the level of the opening in the blast or cupola furnace, at which the charge, along with the fuel consisting of either coal, coke, or charcoal, is introduced; the addition of scrap-iron to the smelting mixture being made at certain works, as at Clausthal, Altenau, etc.; but at Rammelsberg, Andreasberg, etc., the roasted ore or regulus contains sufficient ferric oxide to render the further addition of iron unnecessary. The charge last described yields from 8 to 10 per cent. of an *argentiferous* lead, which is subjected to cupellation for the extraction of its silver and gold, while the *regulus* or *matt* produced in the process, and which is still rich in lead and often in silver, is again roasted after the manner already described, and then resmelted in the cupola blast furnace, by which, in addition to lead and slag, a second regulus is obtained, upon which the process is again repeated, the cycle of operations being usually repeated upon the resulting regulus about four times, when it has become too poor for further treatment.

The lead obtained by these smeltings usually contains a notable proportion of copper and antimony, sometimes also arsenic, whereby the metal is rendered somewhat hard and brittle.

52. Lead Smelting with Basic Ferrous Silicate.—In the Hartz smelting districts the reduction of lead from its sulphur ores, by the direct action of cast or scrap iron, has been largely superseded by the method of reduction with basic ferrous silicate; for which purpose the Rachette blast furnace is employed, the latter having, as indicated in Vol. I., page 89, a long rectangular hearth, with a row of water twyers along each of its longer sides, and a shaft that increases in width gradually from the hearth upwards, while the two ends or narrow sides of the furnace are exactly similar, and each end is provided with a tap-hole for drawing off the metal, regulus, and slag in succession. A basic ferrous silicate available for this process is afforded by the slags of the iron finery, or, as is more generally employed in the Hartz, by an analogous product (slag), produced in the method of copper smelting pursued in the lower Hartz.

In France, etc., silicious ores of lead are smelted with basic ferrous silicate, the process employed comprising two stages; the first stage, or *calcination of the ore*, being effected in a reverberatory furnace, while the second stage, or *reduction*, is effected in the blast furnace, employing *basic ferrous silicates* and lime as fluxes.

The *calcination* of the coarsely-powdered ore is effected upon charges of about 28 ewt. of ore, introduced from a hopper above, on to the red-hot hearth of a reverberatory furnace. The charge having been spread over the bed, the working doors are closed until the whole mass has attained to redness, when rabbling is commenced and continued at intervals of a few minutes, so as to expose every portion of the charge to the oxidizing atmosphere of the furnace, and so to convert the plumbic sulphide into oxide and sulphate, with the escape of sulphurous anhydride. During the *calcination* it is necessary to maintain the contents of the furnace at a dull red heat, and care is required not to allow the temperature to rise sufficiently high to soften or agglomerate the ore, otherwise the process is very much retarded;

but at the end of the calcination the temperature is raised so as to agglomerate the particles of ore previous to their introduction into the blast furnace. The total time occupied in the calcination and agglomeration of a charge is about 8 hours.

The reduction of the roasted or calcined ore is effected in blast furnaces similar to the Castilian furnace, described on p. 139, except that they are a little higher than the latter, and are charged in at the top, which, for this purpose, is closed by a movable plate. The smelting mixture employed in France usually consists of calcined ore, grey slags from the reverberatory furnace, agglomerated lead fume, and basic ferrous silicate (finery slags), the latter constituting about 18 per cent. of the mixture. The furnace being in blast and in working order, the above mixture is then introduced in alternate layers with about 10 per cent. of coke, when the metal and slag collect in the concave hearth of the furnace, the slag running out almost continuously through a tap-hole made in the fore-breast of the furnace, and is received in waggons from which, after cooling, it is tipped, examined for shots of metal, and is then usually thrown away. When the hearth is judged to be filled with metal, the slag-hole is temporarily stopped, and the metal is tapped out in the usual manner into the lead pot, the tap-hole being stopped as soon as the slag makes its appearance, and the lead, after skimming, is then laded into ingot or pig moulds.

LEAD SMELTING BY ROASTING, AND SUBSEQUENT REDUCTION OF THE OXIDIZED PRODUCT IN BLAST AND REVERBERATORY FURNACES.

This method of procedure is pursued in the very extensive lead smelting works of Freiberg, for the treatment of the great variety of argentiferous lead ores occurring in some 900 lodes of the gneissic formation of the vicinity, and which ores are divisible into several classes, according to their geological age and the character of the accompanying gangue or vein-stuff. Of the minerals occurring with the galena in the various ores of the Freiberg district may be noted, iron pyrites, mispickel, zinc blende (ZnS), copper pyrites, vitreous

copper, fahlerz, and various ores of silver, together with a gangue consisting of quartz, calc-spar, fluor-spar, heavy-spar (BaSO_4), spathic carbonate, etc., in very variable proportions. The various ores are mixed together for the smelting operation so as to yield on assay an average of about 40 per cent. of lead, with 15 per cent., or about 49 oz., of silver per ton of ore; and as will subsequently appear, the copper becomes more and more concentrated in each of the three regulii obtained in the process, while copper, as also a little nickel, are frequently extracted therefrom as auxiliary products of the smelting campaign.

53. Freiberg Process.—The smelting operations pursued at Freiberg for the extraction of an argentiferous lead from the above ores are conducted in three stages * :—1^o, *calcination and smelting of certain ores* in blast furnaces; 2^o, *smelting of the regulus* produced in the first operation, also conducted in the blast furnace; and 3^o, *smelting in the reverberatory furnace of the slags* produced in the previous operations, together with certain *argentiferous ores poor in lead*.

The *calcination of the ore* for treatment in the first smelting stage is effected in large double-bedded calciners, in which the flame from the fireplace passes over the lower bed, and then through an opening or flue at its back extremity on to the upper bed, and so forward to the front end of the upper bed before escaping from the calciner; so that in this manner the charge, being introduced at the front end of the upper bed, and gradually raked at intervals towards the opposite end, falls from thence through the opening at the rear end on to the lower bed, and is from thence raked forward towards the front or fire-bridge end of the lower bed, and is thus exposed during its passage through the furnace to a gradually increasing temperature, the final heat of the calcination near the fire-bridge being sufficient to agglutinate or render the mass of ore somewhat pasty; while the temperature of the upper bed scarcely exceeds dull redness. The ore is withdrawn from the fire-bridge end of the calciner, while fresh ore is being continually added at the front end of the upper bed, to supply the place of the charge, as one portion is withdrawn and the remainder raked forward a step;

* Percy. *Metallurgy*, Vol. III.

so that the total charge of the calciner consists of ore in various stages of calcination, according to its position upon the two beds of the furnace. By this method of roasting, the ore is exposed for from 8 to 16 hours, according to the size and exact construction of the calciner, to the oxidizing atmosphere of the furnace; whereby the sulphur is oxidized and largely expelled as sulphurous anhydride (SO_2), while the lead, copper, iron, zinc, antimony, etc., exist in the roasted product almost wholly in the oxidized state. The sulphur remaining in the roasted ore does not usually exceed from 4 to 6 per cent. of the mass, and occasionally falls even lower than the former figure, from which it will be observed that the calcination of the ore is here pushed much further than is necessary when smelting by the English method in the Flintshire furnace, since, as will be observed presently, the object of the roasting at Freiberg is to produce oxidized products of lead, which are then reduced by the carbonaceous fuel of the blast furnace, and not by the reaction of plumbic oxide and sulphide upon each other, as occurs in the Flintshire furnace. In addition to the oxidized products already mentioned, silica constitutes from 15 to 20 per cent. of the roasted product, which further contains alumina, lime, and magnesia in smaller proportions. The calcined or roasted ore thus contains from 20 to 21 per cent. of metallic lead, with from 22 to 26 per cent. of metallic iron, and about 1.5 per cent. of silver.

The product of the calcination is then mixed with one-third of its weight of the *roasted lead regulus* obtained from the smelting of the slags, etc., in the third operation tabulated above; and to this mixture is added 5 per cent. of *fluor-spar* or *lime* and a suitable proportion of *slags*, the latter serving at once to form a "nose" or slag prolongation of the twyer, in the same manner and with a like object to that described in the Hartz process, while its addition also serves for the separation and economising of the shots of lead and regulus that are frequently mechanically entangled in the slag thus employed. This mixture of roasted ore and fluxes, along with the necessary fuel, are now charged into a low blast furnace, the ore mixture being thrown towards the back wall of the furnace, while the fuel (coke) is thrown against the

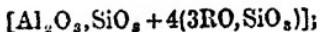
front or fore wall, the proportions of ore to fuel or burthen of the furnace being regulated, as previously described, according to the indications of the "eye" of the furnace, the proper proportion being attained when the "nose" or slag prolongation of the twyers measures from 4 to 6 in. in length.

The blast furnace employed at Freiberg measures about 20 ft. from the twyers to the top of the tunnel head, while the shaft from back to front at the level of the twyers measures about 42 in., and from side to side about 64 in.; and the upper portion of the shaft is divided for a certain distance from the top by a central wall or mid-feather into two shafts. The furnace is supplied with two twyers, introduced through the back wall with a slight inclination downwards, and the hearth projects beyond the line of the front wall, forming a fore-hearth. The shaft is lined throughout its whole height with a refractory lining, and the hearth is formed of three layers; thus in the bottom is first introduced a layer of slags, and upon this is rammed a bed of clay, while above the latter is the working bottom of brasque, well rammed between the furnace walls and the dam-plate, and which is further hollowed out to the form required. The furnace is well drained by suitable channels left in the masonry of the structure; and it is charged, through a pair of apertures near the top or tunnel head, in the same manner as an ordinary cupola furnace; while the *metal*, *regulus*, and *slag*, the products of the smelting operation in this furnace, are tapped out at intervals of about 6 hours through a tap-hole stopped with clay, and situate in the lower part of the front wall or breast of the furnace, from whence the products are received in receptacles placed for their several reception; and in addition to the above products a small quantity of *speise* is also frequently obtained between the metal and regulus.

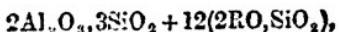
The *reactions* in this furnace are essentially *deoxidizing*, in which the carbon added as fuel constitutes the reducing agent; for the roasted ore introduced into the blast furnace contains, as already noted, lead in combination with oxygen and sulphur, constituting *plumbic oxide* and *sulphate*, of which the former is readily reducible by carbonaceous matters at a moderate temperature (page 73), so that as this oxide descends through the furnace it is quickly and readily reduced by

contact with the incandescent fuel (carbon), and the metal thereby separated will further alloy itself quickly with any metallic silver reduced from the charge either by the direct action of heat alone, or by the joint action of heat and carbonaceous matters; whereby an argentiferous lead separates as one of the products of this stage of the smelting; while the further proportion of lead existing in the calcined or roasted ore, probably as plumbic sulphate, would be reduced at the temperature of, and in the reducing atmosphere of the blast furnace, to the condition of *plumbic sulphide*, which, in combination with variable proportions of iron, copper, zinc, and other metallic sulphides, yields the second product or "*regulus*" above noted; while the *silicious* matters of the charge in contact with the unreduced oxides of iron, copper, zinc, etc., combining with these latter, produce thereby a more or less fusible silicate or *slag* mechanically enveloping more or less of the reduced metal and regulus with which it comes into contact.

The lead obtained from this operation, and known as "*blast-furnace lead*," besides being highly argentiferous is notably hard and impure, containing copper, antimony, iron, etc., and requires purification or softening before it is available for commercial applications. The "*regulus*" from this same operation contains, as its most notable ingredients, about 20 per cent. of lead, with 10 per cent. of copper, 30 per cent. of iron, and 2 per cent. of silver; while the *slags*, which form a large proportion of the furnace yield, retain from 5 to 6 per cent. of lead, with from 5 to 6 oz. of silver per ton, and are formulated by Percy as having a composition represented by



which becomes, according to the notation adopted in this volume,



where RO represents any metallic protoxide.

The smelting of the regulus obtained in the last operation, and which constitutes the second stage of the process as tabulated above, is conducted, in conjunction with *roasted copper ores*, *litharge slags*, *fluor-spar*, and *slags* from the same

operation previously conducted, in a blast furnace similar to that last described, when there results as before an *impure lead*, much impregnated with copper; a *copper regulus* subsequently treated for the extraction of its copper; together with a *slag* consisting essentially of ferrous silicate. The regulus obtained in this stage is again broken up, roasted, and remelted, operations intended chiefly for the concentration of the copper in a third regulus, and of the nickel and cobalt in the speise, each of which products is subsequently treated for the extraction of their respective metals.

The last stage of the Freiberg operations, viz., smelting of the slags, obtained in the first operation, is conducted in a reverberatory furnace of the ordinary type, differing only in minor details of form and construction from those already described. The slag to be smelted is treated in conjunction with about one-half of its weight of the poorer but argentiferous and frequently highly silicious and zinciferous ores of the district, which could not otherwise be profitably smelted; the lead contained in the slags, amounting to about 6 per cent. of their mass, acting as a medium for collecting the silver contained in these poor ores. The ores for mixture with the charge are used, one-half in the raw state, while the other half is previously roasted for the expulsion of sulphur and of zinc, the former element, if too largely present, unduly increasing the amount of regulus produced, while the latter (zinc) in excessive proportions renders the slags too refractory. The smelting charge is spread over the furnace bed or hearth and all apertures are then closed, by which the temperature is raised, and in about 2½ hours the charge is melted, upon which the mass is well rabbled, the doors again closed, and the temperature further increased for some 15 or 20 minutes longer, after which the slag is drawn or skimmed off as completely as possible, and another charge of ore and slag introduced on to the bath of regulus upon the hearth, which is treated as the first charge, the regulus only being tapped out after every third or fourth charge has been thus worked off.

The products of the slag-smelting are an argentiferous *regulus* of lead, copper, zinc, and iron, accompanied by a *slag* consisting essentially of a ferrous silicate, and which is suffi-

ciently poor in lead and silver to warrant its being thrown away or utilised for building purposes.

54. Swedish Method of Smelting Galena.—The argentiferous galena occurring in Sweden, requires a carefully conducted mechanical treatment, consisting of breaking up, picking, and washing, before it is ready for treatment in the blast furnace; and the products separated at each stage of the preliminary operations receive special and specific names.

The treatment of the ore in the blast furnace, or smelting proper, involves two operations known respectively as "raw smelting" and "lead smelting." In the first-mentioned or *raw smelting*, certain poor ores and slimes from the washing apparatus are smelted in conjunction with raw iron pyrites, quartz, slag from the next smelting, and certain furnace residua, in a blast furnace with one twyer, and employing charcoal as the fuel; whereby an *argentiferous regulus* is obtained, accompanied by a useless *slag*, consisting essentially of a ferrous silicate.

In the *second* operation or *lead smelting*, the richer ores and slimes, along with the roasted regulus produced in the first smelting, together with abstrich, cupel bottoms, etc., are treated in a blast furnace along with a proportion of slag from the same operation previously conducted, and a small proportion of roasted iron pyrites; when three products separate, viz., a *highly argentiferous lead* reduced from the galena by the action of the *iron*, separated from the *oxide of iron* (roasted iron pyrites) by the *carbon* of the fuel, and which lead is sufficiently argentiferous to permit of its direct cupellation according to the German method described in page 278, without any previous concentration of the silver by the Pattinson or other process; but the litharge or abstrich first produced in its cupellation is frequently black in colour from the presence of antimony and zinc. Above this lead occurs a *regulus* of ferrous sulphide, resulting from the decomposition of galena (PbS) by iron compounds, as well as from the presence of iron pyrites in the ore; but the regulus also contains in addition zincic sulphide, a small proportion of plumbic sulphide, and a little silver. The third product or *slag* is essentially a silicate of iron, lime, magnesia, and alumina, which has no practical application, except for addition in small

quantities to the blast furnace charge as a flux, whereby the reduced lead is better separated from the extraneous matters of the ore with which it is surrounded.

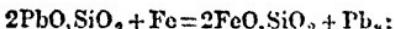
55. Lead Smelting at Pontgibaud, etc., in France.— The special feature of the rich argentiferous galena occurring in this locality is its highly silicious nature, which has given rise to the special method of treatment here adopted, and according to which the ore, after careful dressing and washings, is first *roasted* as completely as possible, for which purpose it was the former practice to employ large double-bedded reverberatory furnaces; the ore being introduced on to the upper bed at the end furthest from the source of heat, from whence it was gradually raked backwards so as to allow it to fall at proper intervals on to the flue end of the lower bed, along which it was raked in the same manner towards the fire-bridges; but the more recent practice is to employ reverberatory furnaces or calciners, measuring* some 40 feet in length, 15 feet in width, and provided with six working doors on each side. The ore is charged from hoppers above the furnace on to the portion of the bed furthest from the fire-grate, where, after the necessary exposure, it is raked forward on to the middle portion of the bed, and, finally, it is advanced on to the portion of the bed nearest to the fire-bridge, and which part is also about 6 inches lower than the other portions. The ore is thus exposed to a gradually increasing temperature, from the point of its introduction until it reaches the fire-bridge, where the heat attained is sufficient to agglomerate or melt the ore, which is then tapped out at intervals of six hours, so that in the last-mentioned calciner three charges will always be upon the bed at the same time; for as the fused ore is tapped out from the end nearest to the fireplace, a fresh charge is introduced on to the coolest portion of the bed.

The effect of this roasting has been to oxidize the lead present in the ore, with the formation of plumbic oxide and a small proportion of plumbic sulphate; while the fusion or agglomeration, as the last stage of the roasting, largely effects the combination of the plumbic oxide with the silicious matters, whereby the lead occurs in the agglomerated ore,

* Phillip's *Elements of Metallurgy*.

to be treated in the blast furnace largely as plumbic silicate.

The roasted and agglomerated ore is next mixed with about 10 per cent. of scrap-iron, 15 per cent. of limestone, together with a small proportion of fluor-spar, lead slags, and lead residua, and treated in a Castilian blast furnace employing coke as fuel, whereby the *plumbic silicate is reduced under the influence of metallic iron and carbonaceous matters*, with the production thereby of metallic lead and a slag of ferrous silicate; thus,



while any plumbic sulphate is at the same time reduced by metallic iron with the precipitation of its lead. The blast furnace thus yields an impure metallic lead containing almost the whole of the silver originally present in the ore, and a slag containing essentially the silicates of iron, calcium, aluminum, magnesium, etc., with the other foreign matters of the ore, and not more than 3 per cent. of lead, otherwise it is remelted; while, when the ore has been imperfectly roasted, a small proportion of *regulus* will also occasionally separate.

The fume collected from the flues is subsequently mixed with silicious ores, roasted in the ordinary calciner, and then smelted with iron, limestone, and fluor-spar in the blast furnace.

56. Smelting of the Ores of Commern.—This is a process pursued at Bleiberg, etc., in Rhenish Prussia, and which is analogous in many respects to the process last described, the ore under treatment being a *galena distributed through sandstone or silicious matters*, and which is accordingly dressed as completely as possible for the separation of sand and silicious matters, after which the dressed ore is *calcined as sweet as possible* by exposing it upon the bed of a reverberatory furnace, after the manner described in the previous article. The ore is introduced into the calciner at the cooler or flue end, and gradually raked forward towards the hotter or fire-bridge end of the furnace bed, where the heat is sufficient to frit or melt the product, with the production as at Pontgibaud of a plumbic silicate, which is then tapped out and becomes the subject of operation in a small blast furnace supplied with four twyers, and burning coke as fuel.

The roasted ore is charged along with about one-half of its weight of puddling furnace slags ($2\text{FeO}, \text{SiO}_2$), a like amount of limestone, and from 8 to 10 per cent. of its weight of *cast-iron*, whereby the melted ore, consisting largely of plumbic silicate, is decomposed, with the production, according to the reactions already indicated, of an *argentiferous lead*, a *lead regulus*, and *slug*.

TREATMENT OF OXIDIZED ORES AND PRODUCTS OF LEAD.

The reduction of lead from oxidized ores, as oxides, carbonates, sulphates, phosphates ("linnets"), arseniates, etc., of lead; or from lead products and residua, as litharge and dross from the English cupellation, the abzug and abstrich produced during the process of cupellation in the German furnace, test-bottoms, and the grey slags produced in the Flintshire or other furnace, which, as already indicated, are frequently rich in oxidized products of lead, are smelted either in small blast furnaces or hearths, or in reverberatory furnaces, in either of which *carbonaceous matters*, or these in conjunction with *iron* or iron-yielding materials, are employed as the reducing agents.

57. Smelting of Plumbic Carbonate, etc.—Plumbic carbonate and phosphate, intermixed in variable proportions, constitute the greenish lumps of ore known in Derbyshire as "linnets." When these compounds occur without any admixture of galena (PbS), they are smelted in conjunction with various slags, impure litharge, cupel bottoms, etc., either in reverberatory furnaces or in small cupola blast furnaces, as the Spanish hearth described on page 139. If the reverberatory furnace be employed, the ore is reduced to a coarse powder and mixed with powdered charcoal, anthracite, or coke, along with fluxes, such as lead slags; occasionally also forge-cinder, together with fluor-spar—if baric sulphate (heavy-spar) be present in the ore—are added to complete the fusion of the gangue. This mixture is spread over the hearth of the furnace, upon which the doors are closed and the temperature gradually raised, while the mass is frequently stirred or rabbled; whereupon the lead is reduced by the action of *carbon* and *carbonic oxide* (CO), and is tapped from the fur-

nace from time to time, while the residue left on the hearth is frequently still sufficiently plumbiferous to require further treatment in the cupola furnace for the extraction of the lead therefrom.

The smelting of these oxidized ores is carried on in Derbyshire, etc., in the cupola furnace known as the Spanish Slag Hearth; for which treatment the ore is reduced to fragments, but not to a fine powder, and in this state it is introduced into the furnace along with coke and various lead slags, the coke being thrown towards the front of the furnace, while the ores, etc., are thrown to the back. The ore is thus subjected to the action of carbon, and carbonic oxide produced by the action of the blast upon the former, which agents effect the complete reduction of these ores at a moderate temperature, with the production of a lead free from phosphorus, and of a *slag*, portions of which may be picked out as still retaining sufficient lead to pay for its profitable extraction, and which are accordingly returned for treatment in the hearth. The lead is either first treated by the Pattinson process for the concentration of its silver before cupellation, or it is directly cupelled for the extraction of its silver. In addition to the lead and slag above noted, a rather large proportion of the metal is volatilised as *fume*, which is however collected in the condensers with which the closed top of the furnace is connected, and is returned to the furnace for reduction with a subsequent charge.

58. Reduction of Litharge.—The reduction of lead from the oxidized products produced during the cupellation of lead, as *litharge*, *abstrich*, *abzugs*, and also from the dross obtained from the Pattinson pots, skimmings from the softening of hard lead, etc., is effected either in reverberatory or in blast furnaces, but in either case using carbonaceous matters, as charcoal or coal, as the reducing agent.

In England and France, at Nassau, Tarnowitz, and other places on the Continent, a reverberatory furnace is employed, in which the bed slopes from all parts towards a tap-hole situated either at one side of the furnace or at one end; and from which, in either case, the metal collected at the lowest part of the hearth overflows a kind of dam formed in the tap-hole, and passes into a cast-iron pot placed outside the furnace,

from which it is ladled at intervals into ingot moulds; while, at the close of the shift or day's work, this dam is broken down, and the separated lead collected on the hearth is tapped out into the lead pot before mentioned.

For treatment in the reverberatory furnace it is not desirable to reduce the litharge to a state of fine powder—the decomposition succeeding best when the particles of litharge and fuel are in the form of small pieces which lie loosely upon the hearth; and it is further necessary that the contact of the litharge with the furnace bottom be prevented as effectually as possible, for which purpose there is first introduced on to the red-hot bed of the furnace, a depth of from 2 to 3 inches of small coal, which undergoes a process of coking during the time that the charge of litharge, mixed with sufficient coal-slack to effect its reduction, is being introduced into the furnace and spread evenly over the bed of coal first introduced. From 5 to 6 cwt. of the smelting mixture is then introduced into the furnace at once, and the temperature is maintained just sufficient to melt the charge, when the litharge suffers reduction, and in from 1½ to 2 hours lead begins to flow over the dam into the lead-pot. The reaction continues to the end of the shift, fresh additions of litharge and coal being made at intervals to continue the supply of lead; while the residue remaining on the hearth after the lead ceases to flow, and which contains the ash of the fuel, along with unconsumed fuel and some unreduced litharge, is then well rabbled at intervals; and the temperature is raised so as to induce a state of semi-fusion in the mass, with the separation of a further small proportion of metallic lead, after which the residue, constituting "litharge slag," is drawn out from the furnace. This product (litharge slag) still retains some undecomposed litharge, and probably also shots of metal; and for the more complete extraction of the metal therefrom, it is subsequently treated in a cupola furnace or in the slag hearth.

The Bleiberg furnace, figured on pages 105 and 106, as also slight modifications of it, are also applied on the Continent to the reduction of litharge, and of the dross derived from the Pattinson pots.

Instead of the reverberatory furnace above described, it is

the practice at Freiberg in Saxony, in Silesia, the Hartz, etc., to effect the reduction of litharge in low cupola or blast furnaces (figs. 23 and 24), which were formerly but some 8 feet in height, but are now built somewhat higher, ranging from 15 to 20 feet from the twyer to the mouth. The hearth is made of a brasque of clay and charcoal or coke well rammed in, and the reduced metal which collects in the hearth passes beneath the fore-wall to the fore-hearth, flowing from thence along a gutter or channel into the receiving pot, into which the lead and slags are tapped at intervals as required; while the charge is introduced through the opening above the fore-wall.

Either charcoal or coke is employed as the fuel in these furnaces, and the blast is supplied through one twyer with a \square shaped nozzle, worked with a small *slag prolongation* or *nose*. The materials of the charge consist of litharge broken into lumps, together with about 15 per cent. of fuel; and if the litharge be impure or mixed with marl, etc., from the substance of the cupel, a small proportion of litharge slags is also introduced into the furnace, the litharge being thrown against the fore-wall and the slags with the fuel towards the back, whereby the lead, which is reduced from its

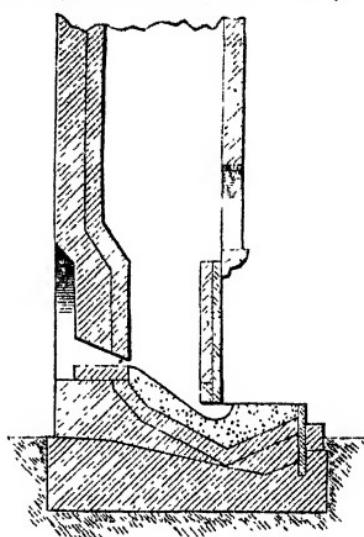


Fig. 23.—VERTICAL SECTION OF BLAST FURNACE FOR REDUCING LITHARGE.

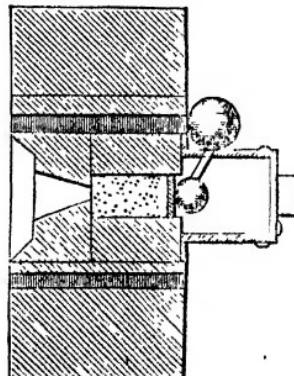


Fig. 24.—HORIZONTAL SECTION THROUGH THE TWYER OF THE BLAST FURNACE FOR REDUCING LITHARGE.

oxide by charcoal at a moderate heat, trickles down towards the hearth, where it collects. The above distribution of the charge facilitates its descent to the hearth, with a minimum duration of contact between the blast and the reduced lead, since prolonged contact of the two would be attended with the reoxidation of the metal. The slags, which should be tough, are usually rich in lead, containing from 20 per cent. to 30 per cent. of the latter, and are accordingly treated in another blast furnace or slag hearth for the extraction of a further proportion of their lead. The amount of litharge that can be passed through one of these furnaces depends much upon its purity—the greater the proportion of foreign matters that it contains, the smaller is the quantity smelted during the day of 24 hours; but from the purer varieties, such as that obtained from the direct cupellation of ore-furnace lead, about 90 parts of lead are extracted from 100 of litharge treated.

59. Smelting of Slags in the English Slag Hearth.—The slags and waste products produced in the Flintshire furnace, the ore hearth, etc., contain, as already indicated, notable proportions of oxidized compounds of lead; and it is the object of the smelting in the slag hearth to extract the metal from these compounds, by treating them with *carbonaceous matters* at a *higher temperature* than is attained when smelting the ore in the Flintshire and other furnaces—the latter condition being necessary for the recovery of the metal.

The slag hearth is a small rectangular blast furnace, of the type known to the Germans as the *Krummofen*, to the French as the *Fourneau-à-manche*, and to the Spaniards as *Pava*. The hearth measures only about 2 feet 3 inches from back to front, and 1 foot 9 inches from side to side, while from the bottom of the hearth to the charging hole is but 3 feet 6 inches, and from the hearth to the arch, which covers or closes the top of the shaft of the furnace, measures from 10 to 12 feet, but these dimensions vary somewhat in different furnaces. The furnace above the hearth is lined with fire-brick, except in front, which is closed above the opening (*a*) (figs. 25 and 26), by the cast-iron plate (*b*), known as the *fore-stone*, and the back of the hearth of the furnace beneath the twyer is formed by a cast-iron plate, the sides of the hearth

being likewise formed by two similar plates, which also carry the side walls above them; while the bottom of the furnace hearth, which slopes forwards and downwards, is formed of a cast-iron *bed plate* (*c*). In front of the hearth is a cast-iron tank or trough (*e*), known as the *lead trough*, into which the metal is run from the hearth; while in front of this again is another trough or *slag pot* (*f*) for the collection of the slag as it flows over from the surface of the metal in the lead trough.

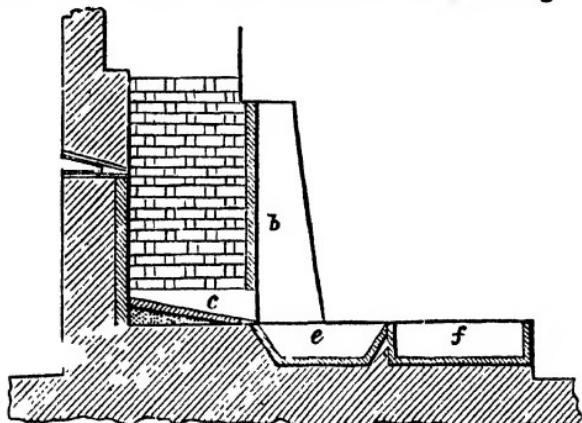


Fig. 25.—VERTICAL SECTION OF THE ENGLISH SLAG HEARTH.

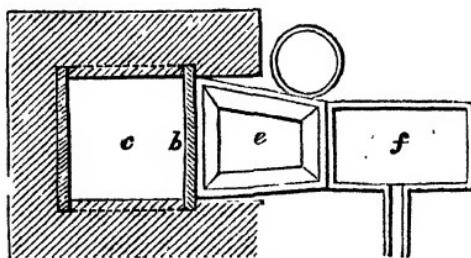


Fig. 26.—HORIZONTAL SECTION OF THE ENGLISH SLAG HEARTH.

In working this hearth it is first slagged out or freed from any adhering slag left from the previous shift, and any badly corroded spots in the lining, etc., are repaired with clay; after which the bottom or *bed plate* of the hearth is covered with a layer of ashes or small cinders to a depth of from 5 to 6 inches,

and made to slope like the bed plate from back to front, but leaving a space between its upper surface and the lower edge of the fore-stone, which space is stopped with clay, with the exception of an opening or tap-hole through which a quantity of the slag flows during the smelting campaign. A quantity of fuel, usually *peat*, is placed upon the hearth thus prepared, and ignited by the addition of a little burning coal, when the blast is turned on and a quantity of coke is then thrown into the hearth. This is succeeded by the addition of a little *slag* or *browse** from a previous shift, until the necessary temperature and working condition have been attained, when the *grey slag* or other residuary product under treatment is thrown into the furnace along with alternate layers of coke,—the distribution and relative amounts of these materials being regulated by the requirements of the furnace, as indicated by its working. As the smelting proceeds, the reduced lead and the accompanying slag descend to the bottom, where the ashes, placed upon the bed plate of the furnace, serve as a kind of filter, through which the lead percolates and passes out from the front edge of the hearth into the tank (*e*) placed in front for its reception, and in the bottom of which is usually introduced a layer of cinders for further separating the metal from any slag passing out along with it. The lead flows from the lead trough (*e*) into a *lead pot*, heated by its own fire, and from which the metal is ladled into ingots, while the slag passing from the hearth along with the lead, accumulates in the lead trough, which it overflows and passes to the slag pot (*f*) already spoken of, and in which it collects; but the greater portion of the slag produced during the process of smelting, passes out from the furnace through an opening made by a bar in the clay stopping between the upper surface of the layer of ashes on the hearth and the bottom edge of the fore-stone, and so passes to the second tank or slag pit, which contains water for the solidification and granulation of the slag, thereby facilitating the separation of any shots of metal carried over by it.

At the end of the shift, when materials have ceased to be added to the furnace, and lead likewise ceased to flow from the hearth, the clay stopping is broken down, and the slaggy

* Lumps of imperfectly reduced ore and slag.

matter remaining on the hearth is raked forward and collected for addition as *slag-hearth browse* at the commencement of the next shift. The shift often lasts about eight hours, of which about six hours is employed in the smelting, and two hours in cleansing out and preparing the hearth for the next shift.

The lead produced in this hearth, and which is known as "SLAG LEAD," is always *hard* and *impure*, from the presence of sulphur, antimony, copper, and iron; since antimony and the other metals occurring so frequently in most lead ores, and which escape, or are only very partially reduced at the lower temperature employed in the previous smeltings, are now reduced by the carbonaceous matters at the higher temperature prevailing in the slag hearth, and thus become concentrated in the metal reduced from the grey slags, etc., produced in the Flintshire and other furnaces—whereby the slag lead requires accordingly to be softened by one of the methods employed for this purpose, as by calcination according to the method to be subsequently described in page 156, before it is ready for the market.

The slag known as "BLACK SLAG" is vitreous, and generally sufficiently poor to be thrown away, unless it should mechanically hold metal in the form of shots, etc., when it requires to be returned to the furnace for its separation.

60. Smelting in the Spanish Slag Hearth.—The furnace known as the Spanish slag hearth or Castilian furnace, is a small blast furnace, of from 3 feet to 4 feet 6 inches in internal diameter, and about 8 feet 6 inches in height. It is circular in section, except at the hearth, where it is prolonged forward by a cast-iron breast pan, provided with a cinder-bed through which the reduced metal filters, and escapes from time to time by a tap-hole into a kettle in which the lead is kept melted for casting into ingots. The shaft of the furnace is surmounted by a rectangular head of masonry supported upon four cast-iron columns, and which contains the door at which the materials of the charge are introduced, as also the aperture by which the gaseous products escape to the flues and fume-condensing apparatus. The furnace is provided with three horizontal twyers, situated one at the back and one at each side of the hearth; and coke forms the fuel employed. This furnace has a very limited application, being only avail-

able in England for the smelting of the poor and readily fusible slags produced in Derbyshire, which thus yield a "rough lead," which requires remelting before sending into the market. Carbon and carbonic oxide constitute the chief reducing agents here employed, while *forge cinder* or other *oxidized product of iron* is also occasionally added as a flux; and if the slag contain baric sulphate, then *fluor-spar* is also added for the same purpose. The reduction in this furnace is exceedingly imperfect, the slag produced being black and vitreous, while frequently containing considerable proportions of lead.

CONDENSATION OF LEAD FUME.

The gaseous current escaping from lead-smelting furnaces carries along with it a very large proportion of *solid* matters rich in lead, and unless some method of arresting these substances be applied between the hearth of the furnace and the stack, the loss of lead from this cause becomes very considerable, besides vitiating the atmosphere in the neighbourhood of the works to a serious and unnecessary degree.

The matters escaping from the furnace are distinguishable as "*smoke*" and "*fume*,"—the former comprising the gaseous products of the combustion of the fuel, and oxidation of the sulphur, etc., in the ore, and will thus contain large proportions of sulphurous anhydride; while the *lead fume*, or solid particles volatilised by the heat, or carried out by the blast or draught through the furnace, contains (besides carbonaceous matters, silica, ferric and zincic oxide, lime, alumina, particles of ashes, etc.) considerable proportions of plumbic sulphide, oxide, sulphate, and carbonate, together with more or less silver, and which, therefore, if allowed to escape into the atmosphere, involves a very serious loss of metal, amounting in exceptional cases to as much as 10 per cent. of the total yield of the ore.

At Pontgibaud, about 3·67 per cent.* of the lead contained in the ore is subsequently extracted from the *fume* collected from the condensing apparatus connected with the blast furnaces there employed; but the lead reduced from "*fume*," like that from the "*slags*," is, however, usually less argentiferous than that extracted directly from the corresponding ores.

* Phillips. *Elements of Metallurgy.*

ANALYSES OF LEAD FUME.

OPERATION,	Reverberatory Furnace and Slag Hearth.	Reverberatory Furnace.		Re- fluxery.	Blast Furnace.	
		Pontgi- baud.	Alston Moor.		Frei- berg.	Pontgi- baud.
LOCALITY,	Bagillt.	Rivot.	Berthier			
ANALYST,	Percy.					
Plumbic Oxide,	46·54	...	10·20	48·30	27·90	10·00
" Sulphate,	4·87	39·00	65·60	...	13·00	47·00
" Carbonate,	35·00
" Sulphide,	4·50	1·40
Arsenious Anhydride } (As ₂ O ₃),	1·50	...	14·40	2·10	...
Ferric Oxide,	4·16	...	3·40
Alumina,	4·16
Zincic Oxide,	1·60	2·70	13·80	25·70	49·50	10·00
" Sulphate,	2·30
Lime,	6·07
Sulphuric Acid,	26·51
Silica,	13·20	5·60	33·00
Clay,
Oxide of Antimony,	3·90
" Bismuth,	0·50
Carbonic Anhydride,	4·50	7·00	...
Insoluble Residue,	10·12

Numerous methods have been proposed for retaining and collecting this lead fume, amongst which the most simple and effective plan is to pass the smoke and fume through a long, slightly inclined, *straight* or *tortuous flue*, placed between the furnace and the stack, which latter must be of sufficient height to produce the draught required for the furnace with which it is connected. The flues constructed for this purpose are of brickwork, arched over at the top, and are of large dimensions, measuring as constructed in the north of England, as much as 8 feet in height and 9 feet in width, while a single flue extends for a length of 4451 yards, or more than 3½ miles, and examples are recorded of the condensing flue of a single mill measuring upwards of 5 miles

in length, while the combined flues of a single work exceed 8 miles in length. Owing to the large sectional area of these flues, the velocity of the gases from the furnace becomes considerably reduced, an effect which is further promoted by the cooling of the gases in their passage through these flues to the stack, and this reduction in velocity favours materially the deposition of the very finely-divided solid matters held in suspension by the gaseous current from the furnaces; also the large surface, exposed by the walls of the flues, likewise acts by friction in arresting the solid particles constituting lead fume. The flues are cleaned out at intervals, access being obtained to them by taking down a portion of the brickwork, when men are able to enter and extract the collected fume, which is treated as already described, for the extraction of lead, which thus forms in the larger works a considerable item of economy, and in many instances more than repaying the cost of the condensing arrangement, while at the same time freeing the surrounding atmosphere from the poisonous vapours of lead compounds. To obviate the expense of constructing and maintaining these long flues, which further can only be constructed in certain localities where the required length can be obtained, as for instance on the side of a hill, when the flue assumes a tortuous course along the slope; various other plans have been proposed, such as to pass the fumes through large *condensing chambers*, through which the direct passage of the vapours from the one side to the other is prevented by the introduction of a series of diaphragms connected alternately with the top and bottom of the chambers, and around which the fumes and smoke are required to pass before quitting the chamber at the opposite end to that at which they entered; others again propose to expose the fume to the action of an *artificial rain* or *steam*, or to draw the fumes, etc., through water by the application of various *methods of exhaustion*, and to these latter classes belong the condensers of Stagg, Stokoe, etc.

61. Stagg's Condenser.—In this condenser the *fume* is condensed in water placed on the bottom of a large rectangular chamber or cistern, divided into a series of compartments by a number of vertical partitions connected alternately

with the top and bottom of the chamber, whereby the fumes and smoke from the furnaces, entering by a flue at one end of this chamber, are made to pursue a circuitous course through the series of compartments into which it is divided; and at each passage, from the bottom of one compartment to the next, the fume passes through a definite column of water, regulated by the depth to which the dividing partition dips below the surface; while the required exhaustion, for drawing the fume through the water, etc., is provided by connecting the exit flue with one or more air pumps or exhausting machines. The water in this manner becomes charged with the fume, and is drawn off at intervals into tanks, where the fume is allowed to subside.

62. Stokoe's Condenser.—This arrangement is in use at Langley Mill, at the Keld Head Smelting Works, etc., and consists of two rectangular chambers *a*, each of which is divided into compartments by vertical partitions, which alternately reach to the top and dip beneath the surface of water on the bottom of the condenser, the chamber being further divided horizontally by two floors *b b*, formed of planks about 3 inches square, on which is placed a thin layer of faggots, thorns, pebble stones, or other filtering material.

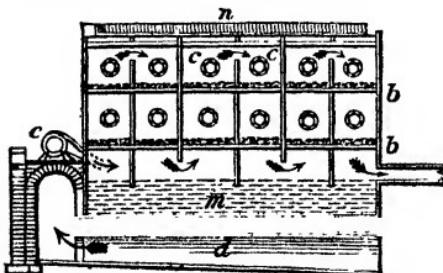


Fig. 27.—LONGITUDINAL SECTION OF STOKOE'S CONDENSER.

Fig. 28.—TRANSVERSE SECTION OF STOKOE'S CONDENSER.

The condenser is thus divided into eighteen small chambers or compartments, into each of the upper twelve of which access is obtained by small doors *c c*. On the top of the condenser is a water cistern *n*, which supplies water to a series of perforated zinc pipes in the upper tier of chambers,

and by these means a fine rain is continually falling on to the filtering beds. The fan (*e*) withdraws the fume from the furnace along the flue *d*, and then drives it through the whole series of chambers in both condensers, during its passage through which it is exposed to the condensing action of the fine rain or dropping water previously mentioned, and to the filtering action of the layer of faggots upon the floors, which latter are further cleared from the condensed fume accumulating on them by the water falling as rain upon them, whereby the filtering power of the beds is preserved from the choking and stoppage which would otherwise occur, while the fume is collected thereby in the water *m*, in the bottom of the condenser, which is drawn off at intervals, as in the last arrangement, and the solid matters allowed to settle.

SEPARATION OF SILVER FROM LEAD.

As already noted, *all* galenas are more or less argentiferous, and during the smelting of these and other ores of lead any silver which accompanies them is reduced simultaneously with the lead, producing thereby an argentiferous lead, which product then becomes the object of a special treatment for the separation of the silver. For this purpose three methods are or have been generally used, these are the methods of "*cupellation*," the method introduced by Mr. H. L. Pattinson and known as the "*Pattinson process*," and the plan proposed by Mr. Parkes for the *desilverization of lead by means of zinc*.

63. **Pattinson Process.**—The *method of cupellation*, details of which are supplied on p. 273 was substantially the only operation employed for the separation of silver from lead, prior to the introduction of the Pattinson process in 1829; and while it was not considered practicable or profitable to extract, by cupellation, the silver from argentiferous lead when the former was present to a less extent than about 8 oz. per ton of metal, yet, by the introduction of the Pattinson process, the silver can be profitably extracted from lead when present only to the extent of from 2 to 3 oz. per ton of metal, while the lead, after Pattinsonization or desilverization by this method, retains only from $\frac{1}{2}$ to $\frac{2}{3}$ oz. of

silver per ton, and the desilverised lead is further much improved in quality by the treatment.

The *Pattinson process* has for its object the concentration of the silver in a smaller proportion of lead, or the separation of a more highly from a less highly argentiferous lead; and it is founded upon the fact, discovered by Mr. H. L. Pattinson of Newcastle, that if an argentiferous lead be melted, and subsequently cooled slowly and uniformly, the mass being at the same time carefully stirred, there separates a mass of small crystals, which may be removed, leaving the more fusible metal in the vessel. An examination of the two portions reveals that while the *crystals are much poorer in silver* than the original lead, the *fluid portion* has been correspondingly *enriched in silver*, and thus, by a repetition of this process again and again upon the two products, the original lead can be divided into two portions, the one very considerably impoverished, or retaining but from $\frac{1}{2}$ oz. to $\frac{3}{4}$ oz. of silver per ton, constituting the commercial lead, while the other and smaller portion will be considerably enriched, the degree of concentration depending upon the richness of the original lead treated. For the final separation of the silver from the enriched lead, it is subjected to cupellation, and since this operation involves a loss of about 5 per cent. of the lead treated, the Pattinson process obviously effects a considerable economy of lead in the cupellation stage, since only about $\frac{1}{5}$ part of the original lead is treated in the cupel for the separation of the full amount of silver.

The products of the Pattinson process then, are—1°, A *commercial lead* much improved in malleability, ductility, and softness by the treatment, owing to considerable proportions of the impurities, as copper, nickel, antimony, arsenic, etc., of the original lead either passing into the concentrated rich lead during the crystallization of the metal, or are oxidized and removed in the dross or skimmings; 2°, a *very rich lead* for cupellation; and 3°, a proportion of *dross or skimmings*, resulting from the oxidation of the metal by the atmosphere during its exposure for the conduct of the process.

For the conduct of the Pattinson process a series of from seven to eleven hemispherical cast-iron pots or kettles, *a*, fig.

29, of about 5 feet in diameter, and each capable of holding about 9 tons of metal, are arranged in a single row along one side of a building; each pot being heated by its own fire (*b*), and supplied with independent flues (*c*) running quite around the bottom of the pot, except at the front, where it communicates with the fire *b*; each fire is also provided with its own damper, so that any pot can be cooled down without interfering with the remainder, while the flues, from a row of furnaces, all communicate with a common stack. *d* is the level of the floor upon which the workman stands, and *e* is the level of the floor on the opposite side of the pots, beneath which is a passage for obtaining access to the fires, ash-pits, etc.

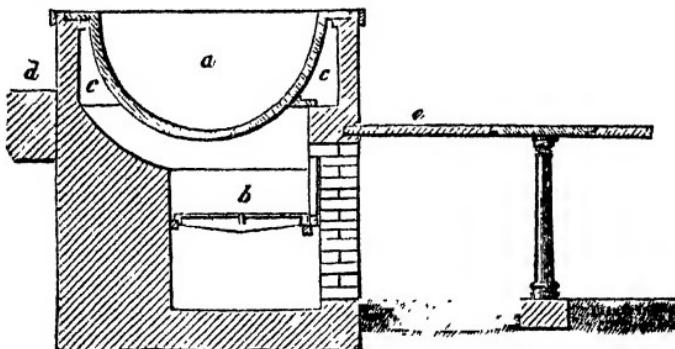


Fig. 29.—TRANSVERSE VERTICAL SECTION OF THE PATTINSON POT.

The number and capacity of the pots arranged in one row varies in different localities, according to the nature and degree of richness of the lead to be treated, thus with *poor* leads, *i.e.*, such as contain only small proportions of silver, it is the practice to remove from any pot a larger proportion of the lead as crystals, than is practised when richer varieties of lead are the subject of operation; and hence a smaller number of pots are required for the treatment of such leads if treated alone, although the desilverization is not so perfect as when smaller proportions are removed at each stage, and a larger number of pots employed; so that while pots of 10, 12, or 15 tons capacity are employed in the Hartz, Silesia, etc., yet in other localities, pots as small as 3 tons capacity have been employed. In addition to the lead pots

above mentioned, there is built between each pot, as shown on fig. 30, a smaller pot known as the *wash-pot*, in which a quantity of lead (having the same content of silver as its adjoining pot), is kept melted for the purpose of heating the crystallising ladles, and cleaning the holes, when they become stopped from the solidification of the lead in them, during the draining of the crystals. The crystallising ladle above



Fig. 30.—**PLAN OF THE ARRANGEMENT OF THE PATTINSON POTS.**
mentioned, employed in removing the crystals of lead from any pot, is of iron, except from *a* to *b*, which forms a handle of wood; the bowl of the ladle is about 18 inches in diameter and 5 inches deep, and perforated over its under surface with a number of holes of some $\frac{1}{2}$ inch in diameter; but when cranes are applied to the working of the pots, then the ladles are made of 20 inches in diameter, and $6\frac{1}{2}$ inches deep.

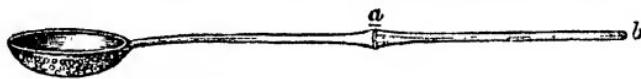


Fig. 31.—**CRYSTALLISING LADLE EMPLOYED IN THE PATTINSON PROCESS.**

In commencing the Pattinson process, the charge of pig lead is introduced into the middle pot of the series to be employed, which, if the lead contain from 10 to 12 oz. of silver per ton of lead, requiring five or six crystallizations (Pattinson)* for its concentration, will be the fifth from the end, and the charge employed usually weighs from 7 to 9 tons. The lead is now melted as rapidly as possible, and heated to a temperature a little beyond the point required to effect its complete fusion; when the fire is withdrawn, and the oxides, etc., skimmed from the surface by a perforated ladle, allowing the fluid lead to run through while retaining the unfused oxides, which are placed upon one side for subsequent reduction. The surface of the metal in the pot being now quite clean, the damper is put down and the whole cooled, to facilitate

* Percy. *Metallurgy*, Vol. III.

which, if much too hot, a small quantity of water is projected upon the surface, while, as the metal cools, the workman continually stirs the mass with an iron rod, transferring any crusts of metal that form on the surface, or become attached to the sides, towards the middle of the melted mass. As the temperature falls, the contents of the pot begin to thicken, from the separation throughout the mass of crystals of a less fusible alloy of lead, upon which the crystallising ladle already described, and which has been previously heated by immersion in the wash pot already mentioned, is introduced by the workman, who pushes it to the bottom of the pot, and then raises it up out of the bath by applying his weight at the extremity of the long handle; while a pig of lead placed on the edge of the pots acts as a fulcrum, upon which the ladle can be jerked so as to accelerate and more completely drain the fluid metal from the surface of the crystallised portion contained in the ladle. When after thus thoroughly draining the crystals contained in the ladle, the workman transfers the contents of the ladle to the next pot on the right, or No. 4; and in this manner, the bath being continually stirred to facilitate the cooling and prevent the aggregation of the crystals into one mass, the lead is crystallised and ladled out until about two-thirds of the contents of No. 5 have been transferred to No. 4, when the remaining one-third is transferred to the next pot on the left, or No. 6. After the removal or transference of a ladleful of crystals from one pot to the next, the ladle is warmed, and the holes cleaned out from any solidified lead by immersion in the corresponding wash pot, before it is reinserted into the metal undergoing enrichment or crystallization. The working or crystallising of the contents of each pot occupies about two hours.

The crystallised metal transferred to No. 4 is found to contain, approximately, 5 oz. of silver per ton when treating lead of 10 oz. per ton in No. 5; while the one-third transferred to No. 6 will contain about 20 oz. of silver per ton. The pot No. 4, supposing it to be empty at the commencement, now contains two-thirds of its charge, and this is made up to a full charge by the addition of lead, assaying the same amount of silver (i.e., 5 oz. per

ton), if such be at command; or No. 5 is again charged and the concentration repeated, at the end of which, No. 4 will contain approximately $\frac{2}{3} + \frac{2}{3} = \frac{4}{3}$, or one-third in excess of the full charge, and this or a smaller proportion is withdrawn before proceeding to the crystallization of No. 4, the portion so removed serving to make up the charge of this pot at a subsequent crystallization according to the method first indicated. No. 4 is now treated exactly as No. 5, i.e., the lead is melted, cooled, crystallised, and the crystals drained and ladled out, until two-thirds of its contents, yielding only about $2\frac{1}{2}$ oz. of silver per ton, has been transferred to No 3, and one-third containing 10 oz. of silver per ton returned to the left, or to No. 5; and in this manner, as each pot becomes filled either with metal transferred from the adjoining pot, or by the addition of lead of the same assay as that which it contains, it is then subjected to the same cycle of operations; in every case the impoverished crystals being gradually transferred to the next pot on the right, while the enriched lead or mother liquor is transferred at each step to the next pot on the left; the portion transferred to the right being in each case impoverished to the extent of about 50 per cent. of its silver, while that transferred to the right is enriched to a corresponding amount, until the metal in No. 1, or the extreme pot, at the right hand side, and known as the "*market pot*," contains lead, with only some 10 or 15 dwts. of silver per ton, and is sufficiently pure to be directly cast into ingots, and sent into the market as commercial lead; while the extreme pot at the other extremity of the series will usually contain a lead with from 150 to 259 oz. of silver per ton, constituting the metal to be subjected to cupellation.

It is possible, however, to continue the concentration of the metal by this process, until the enriched lead contains between 600 and 700 oz. of silver per ton; beyond which limit, however, it does not appear practicable to effect the concentration. To attain the last degree of concentration, at some establishments the manipulation is slightly varied in the last stages, according to which, it is the practice, instead of lading out the crystals from the last working pot, to continue the stirring as before until the metal thickens, then to draw the thickened or crystallised metal towards the sides of the

pot, thus forming a cavity in the centre, into which the more fluid and highly argentiferous lead drains; then by introducing the perforated ladle and pressing it down upon the thickened metal, the more fluid lead drains, and is squeezed into the ladle, from which it is ladled out by a second, but plain or nonperforated ladle; and by these means a higher degree of concentration is attainable, than by strict adhesion throughout to the previous plan.

The crystallization of the contents of a single pot at once is described above; but it is to be understood that two pots in the same row are frequently under operation at the same time, that is, while the once impoverished lead in No. 4 is under treatment, at the same time the once enriched lead in No. 6 may be under treatment, each transferring a portion of their contents to No. 5, while a further portion passes respectively to Nos. 3 and 7, and so on for the pots higher and lower in the series, the pots being treated in a regular sequence, the order of which is regulated so as to obviate as much as possible the necessity for adding fresh lead to make up the charge of intermediate pots prior to the crystallization of their contents.

The exact charges and mode of procedure observed in the conduct of the Pattinson process, vary at almost every establishment; that is, the order in which the pots are crystallised, and the manner in which the charge is made up to the full weight required previous to commencing the crystallization, differ at various works; also the exact proportion removed in crystals at each stage usually varies between the above named limit of two-thirds of crystals to one-third of fluid lead, or method of *thirds*, and seven-eighths of crystals with one-eighth of fluid enriched lead, constituting the method by *eighths*. The latter method, as already indicated, being however most generally applicable to the treatment of a lead having a low content of silver.

At the silver-lead works of Tarnowitz, where about 15 tons of metal is heated in each pot, the operation of skimming, crystallising, and lading out the contents into the two adjacent pots, occupies about $2\frac{1}{4}$ hours (Teichmann); but the duration of the process is influenced by the purity of the lead, since the presence of impurities, such as copper, antimony,

arsenic, etc., cause the crystals to be generally smaller, and the draining slower, attended accordingly with a lengthened duration of the process, and necessitating an increased number of crystallizations to impoverish the lead to the required degree.

The *loss of lead* also varies with the quality of the metal operated upon; but for lead containing about 8 oz. of silver per ton, this loss amounts to some 12 or 14 lbs. per ton (Percy), (exclusive of that converted into litharge), and which is subsequently recovered according to methods similar to those stated on page 133, for the reduction of litharge. Throughout the Pattinson process the heated lead undergoes oxidation, and a considerable proportion of dross or skimmings is produced, consisting largely of litharge (PbO), accompanied by smaller quantities of other oxides resulting from the partial oxidation of the foreign metals contaminating the original lead. But the amount of skimmings so obtained varies with the number of crystallizations to which the metal is subjected, and will thus increase with the poor ness of the metal; but for a lead assaying the above amount of 8 oz. of silver per ton, the yield of skimmings will form about 20 per cent. of the charge.

To aid in the manipulation of the heavy ladle employed for baling out the crystals, it is not unusual to erect a small jib-crane in front of the pots, of such dimensions that a small roller at the end of the jib stands a little above the level of the top of the pots, and serves as the fulcrum for raising the bowl of the ladle with its contents of crystallised lead above the surface of the metal, while an arrangement at the other end of the jib, directly above the crane-post, permits of the ready insertion of the extreme end of the handle of the ladle into a kind of cap, so that the ladle is held horizontal, and the liquid lead drains from the crystals without any further labour of the workman; while the roller in front, on which the ladle handle rests, also serves as a convenient support upon which to rock or jerk the contents for the better and more complete draining of the crystallised metal; and by rotating the crane the ladle is brought over the next pot, and its contents readily discharged into it.

At Rouen and elsewhere, machines have been introduced for stirring and crystallising the pots; according to which the pots are arranged so that a vertical stirrer, driven by a belt, agitates the metal in the pot; the rotation of the stirrer being continued until the desired proportion (two-thirds) of the charge has assumed the crystalline form, when, by opening a slide valve in the side of the pot, the fluid, enriched lead, is drawn off into another vessel, to be returned to the next melting pot for further concentration.

64. Parkes' Process.—This is a method of desilverising lead based upon the superior affinity of silver for zinc than lead, and the almost complete separation of zinc from lead when the two are melted together, and subsequently cooled slowly; whereby if argentiferous lead be fused with metallic zinc, the two being well stirred together, and the mass then allowed to cool slowly, the zinc will separate largely and form a distinct layer or stratum upon the surface of the lead beneath, while the zinc crust thus formed will have further abstracted almost the whole of the silver from the lead; and as the result of the operation, there is formed an *highly argentiferous crust of zinc*, containing also a little lead, and beneath which is a layer of *poor lead* almost desilverised, but retaining a small proportion of zinc, rendering such lead hard and unfit for most applications without subsequent softening or improving.

At Llanelly, where this process was introduced, the charge of from 6 to 7 tons of argentiferous lead was melted in the iron pot or kettle *a*, resembling the ordinary Pattinson's pot, while the zinc to be added was melted in a smaller adjacent pot *b*. After melting the lead, it is skimmed and its temperature raised to the melting point of zinc, when from $1\frac{1}{2}$ to 2 per cent. of the melted zinc, according to the content of silver in the lead, is poured into the molten lead, the incorporation of the two being effected as thoroughly as possible by continued stirring of the mixture, after which the fire is lowered, and the mass allowed to cool slowly; the thick ring of zinc which tends to form around the edge of the pot being continually removed by a piece of wood, until, when a tolerably uniform crust of zinc forms over the surface, it is removed by a perforated ladle, an operation which is repeated upon succeeding

crusts until the subjacent lead indicates, upon assay, a sufficiently low content of silver.

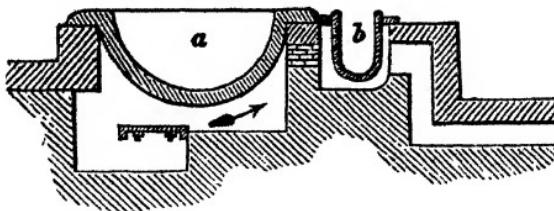


Fig. 32.—POTS FOR MELTING LEAD AND ZINC IN PARKES' PROCESS.

The separated crusts of argentiferous zinc, containing also a little lead, are then heated in the liquation retort *d*, fig. 33, to a temperature somewhat above the melting point of lead, whereby a quantity of *argentiferous lead*, containing a little zinc, will liqueate out and collect in the receptacle *c*, and may be again returned to the pot *a*, for subsequent

treatment with a further proportion of zinc; or it may retain sufficient zinc to permit of its being remelted, skimmed, and then cooled, when a second argentiferous crust will separate; or it may be sufficiently rich to be treated directly for the separation of its silver by the process of cupellation. The residue collected from the retorts (*a*) is then mixed with lime and carbonaceous matters, as coal, etc., and *distilled in retorts or crucibles for the separation of the zinc*; after which the residue remaining contains the *silver* along with lead, some copper, etc., together with certain pulverulent and earthy matters. The highly argentiferous lead so obtained is then remelted, skimmed, and cupelled for the extraction of the silver.

There is a loss of lead in Parkes' process amounting to

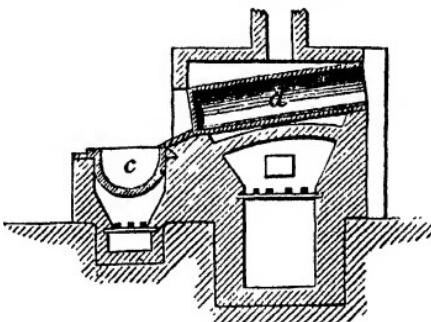


Fig. 33.—LIQUATION APPARATUS FOR PARKES' PROCESS.

about 1 per cent. of the metal treated. Instead of adding the total charge of zinc all at once, as above described, it has been proposed to make the addition at two or three times, separating a portion of the silver in a zinciferous crust between each addition; thus in Carinthia a first addition of zinc to the extent of about $\frac{3}{4}$ per cent.* of the weight of the lead is made, the mixture well stirred, and after the necessary rest and cooling, a first argentiferous crust of zinc is removed, when the operation is repeated with the addition of about $\frac{1}{2}$ per cent. of zinc; and, lastly, $\frac{1}{2}$ per cent. of zinc is added, and a third crust separated.

The lead remaining in the pot after the separation of the zinc crusts is run into a reverberatory softening furnace, the bottom of which is a flat iron pan, in which the metal is melted, thereby oxidizing the zinc, antimony, iron, etc.; the *dross*, etc., which rises to the surface being skimmed off at intervals, until the lead has acquired the necessary degree of softness, as indicated by samples withdrawn from the charge. The softening is often finally completed by subjecting the metal to a species of *poling*, in which a piece of wood is inserted into, and kept below the surface of the melted lead contained in a suitable pot, similarly to the process described for poling tin, Vol. I., page 204.

65. Flach's Method of Desilverization by means of Zinc.—A modification of Parkes' process has been patented by the late C. F. Flach, and has been introduced into practice at several of the English and Continental lead-smelting establishments, with a reported economy over the Pattinson process. The modified process of Flach consists in melting the charge of lead in large cast-iron pots, and adding the zinc in three successive charges; thus, when the lead is melted, about two-thirds of the total charge of zinc is added, and the mixture well stirred; after which the fire is lowered, whereupon a zinciferous crust rapidly forms, and is removed by skimming with a suitable ladle; the skimming being continued until the lead begins to crystallise, upon which the heat is again raised, and a second portion of about one-fourth of the charge of the zinc is introduced, and the above operations of cooling and skimming are repeated, after which the

* Percy. *Metallurgy*, Vol. III.

remaining portion of the zinc is added, with a repetition of the same treatment. These zinciferous crusts are then treated in smaller pots for the liquation of a portion of the lead, which collects in the bottoms of the pots, while the concentrated alloy is skimmed from its surface. The concentrated zinciferous alloy thus obtained is now smelted along with lead slags and tap cinder in a small blast furnace, whereby the zinc is largely volatilised as zincic oxide, while a highly argentiferous lead is obtained, which is then directly subjected to cupellation for the separation of the silver.

SOFTENING OF HARD LEAD.

Lead, as reduced from its ores, is usually contaminated more or less with *antimony*, *copper*, *tin*, *arsenic*, and other impurities, the extent of impurity varying with the kind and quality of ore from which the metal has been reduced; thus *slag leads*, and especially lead reduced from Spanish ores, are more or less hard and deficient in malleability from the presence of these impurities. Such lead accordingly requires to be "softened" or "improved" to fit it for application to the uses of the arts and manufactures. The metals above enumerated as imparting hardness to lead are readily oxidizable, and the various methods of softening lead are operations for effecting their oxidation, either by atmospheric oxygen according to the manner generally pursued, or by the

ANALYSES OF HARD LEADS.

LOCALITY.....	England.	Spain.	Freiberg.	Andreasberg.
Lead,.....	99.27	95.81	91.51	77.75
Antimony,.....	0.57	3.66	5.32	21.27
Arsenic,.....	1.02	...
Copper,.....	0.12	0.32	0.90	0.16
Iron,	0.04	0.21	0.62	0.42
Zinc,.....	0.20	...
Sulphur,.....		
	100.00	100.03	99.57	99.60

addition of oxidizing materials, as alkaline nitrates, chlorates, hypochlorites, etc., to the charge of molten lead to be softened.

66. Softening of Lead by Oxidation.—The method of softening by atmospheric oxidation or calcination is conducted in a reverberatory furnace with a low arch or crown, and fitted with a shallow cast-iron bottom *a*, indicated in figs. 34 and 35, or

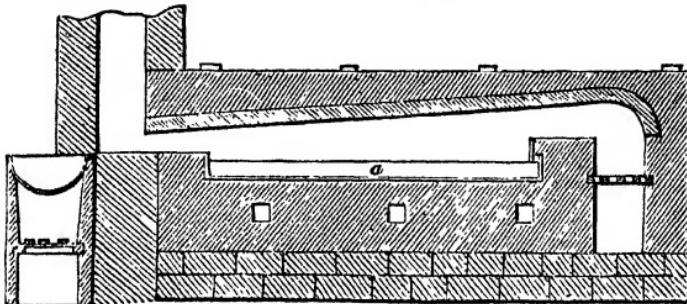


Fig. 34.—SECTIONAL ELEVATION OF SOFTENING FURNACE.

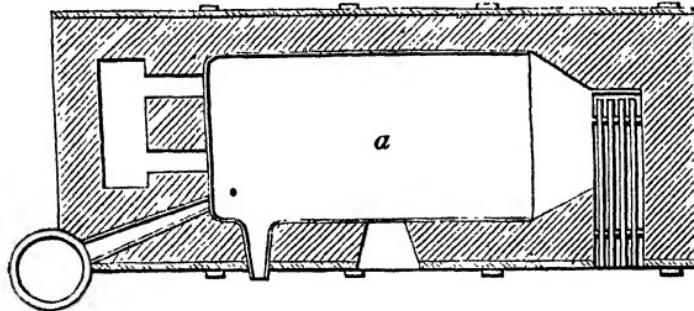


Fig. 35.—PLAN OF THE BED OF SOFTENING FURNACE.

other bottom, formed so as to be impervious to the percolation of molten lead. The charge of from 6 to 10 tons of lead is either melted in an adjoining pot before its introduction into the softening furnace proper; or the pigs of lead may be at once inserted upon the hearth of the furnace and there melted, upon which the temperature is raised above the melting point of lead, and thereby the more oxidizable metals, as antimony, arsenic, copper, tin, etc., along with some lead, are oxidized, and collect as a kind of dross or slag upon the surface of the metal, when

the temperature is lowered, and the dross is raked or skimmed off. The heat is now again increased with the production of a further proportion of dross, when the temperature is lowered as before for its removal by skimming, and these operations of oxidation and of skimming off the dross are repeated until specimens of the metal taken out for trial exhibit the required degree of softness and malleability; the surface of the metal in the furnace also generally indicating this condition by presenting a blue iridescent colour and crystalline texture, instead of being rapidly covered with a dull bluish-white incrustation of oxide of antimony, as presented by the hard metal.

The duration of the softening process depends upon the purity or relative hardness of the original lead. Thus, while from eighteen to twenty-four hours will suffice to soften some varieties, others and more impure specimens, such as those produced from the smelting of lead slags in the slag hearth of Derbyshire, or the hard lead produced from Spanish ores, requires considerably longer time to soften, the period in such cases extending to some fourteen days of constant attention.*

At Freiberg, in Saxony, the softening is effected in a reverberatory furnace, to the hearth of which a blast of air is supplied by a pair of twyers for the oxidation of the impurities.

The *slag* or *dross* removed from the surface of the metal during the softening process differs much in physical qualities, but often presents a dull brownish colour, is hard and heavy, consisting as previously indicated largely of the oxides of antimony, copper, tin, lead, etc., and if treated along with carbonaceous matters in a blast or reverberatory furnace, it yields a *hard* lead, from which, however, a proportion of soft lead may be obtained by subjecting it to a repetition of the above softening process; or such hard metal may be at once employed as an inferior metal for the manufacture of bullets, inferior type, etc.

SHEET-LEAD, ETC.

The chief applications of metallic lead to the arts are in the form of sheet-lead for roofing, for the lining of sulphuric acid chambers, etc., and as lead piping or rod. Sheet-lead was

* Makin. *Manual of Metallurgy*.

formerly prepared by casting the metal in a suitable mould, the required thickness being regulated by a *strickle* resting upon the sides of mould, and moved by workmen over the length of the sheet, so as to remove the excess of fluid metal; but the more modern practice is to cast the metal as a thin slab, which is then rolled out in its *cold* state between cast-iron rollers, of some 18 inches in diameter, and provided with reversing gear, whereby when the sheet or slab has passed through the rolls from left to right, by reversing the mill the sheet again passes between the rolls in the reverse direction; the apparatus is also provided with a hand wheel actuating screws, by which the rollers can be brought closer together, and the thickness of the plate reduced at each passage between the rolls. As the sheet extends in size beyond the limits of the rolls, it is cut up into smaller squares, upon each of which the rolling operations are continued until the metal has acquired the desired degree of thinness; and for the production of very thin sheets it is a practice, in the last stages of the process, to pass two or more thicknesses of metal properly prepared through the rollers at once.

Lead pipes were formerly made by casting the metal in a mould around an iron core, and subsequently drawing the tube with its core through a succession of steel dies, continually diminishing in size, whereby the metal was caused to *flow* along the surface of the core, and thus the length of the pipe was increased with a corresponding decrease in its diameter; but at many works lead piping, as also the *lead rod*, required for various purposes, as bullet making, etc., is prepared by the operation known as "*squirting*" lead, in which the metal, contained in a large cylinder, is forced or squirted by the action of hydraulic pressure upon the metal, through a hole or die-plate of the required size and form, fitted in the upper end or cover of the cylinder; and according to this method, by altering the dies through which the metal is squirted and the amount of metal operated upon, rods of any required length may be readily manufactured. The metal to be manufactured into pipes or rods is melted and poured in the desired quantity into an iron cylinder, into the bottom of which fits the end of a ram or plunger, the other extremity of which fits into a hydraulic cylinder beneath. The aper-

ture for the introduction of the metal having been stopped by a screwed plug, and a suitable die applied in the upper end of the cylinder, the pressure is then applied to the ram, and the metal flows or is squirted through the die, which, if lead pipe is being produced, is also fitted with a spindle, of the size of the inside of the pipe, and around which the metal flows, forming a hollow tube or pipe. The metal in the cylinder is kept heated to a point just below fusion during the squirting operation, the heat being applied by a fire or other heating apparatus applied around the outside of the cylinder containing the lead.

Lead-rod or lead-wire, owing to the inferior tenacity of the metal, could not be manufactured according to the ordinary methods of wire-drawing, and it is therefore necessary to have recourse to the operation of squirting, and to make use of the flowing quality of the metal.

In the manufacture of lead pipes, rods, etc., the purest and softest of lead is not usually required, since the admixture of a little antimony or tin hardens the metal, gives to it a brighter colour, and enables it to stand wear somewhat better.

CHAPTER III.

ZINC.

THIS metal, which is known commercially also as "*spelter*," is a bluish-white metal, possessing when polished a bright metallic lustre. Commercial cast-zinc is brittle and crystalline, but the pure metal is malleable and may be hammered into thin leaves at the ordinary temperature; while the commercial metal is brittle when cold, but becomes malleable if heated to a temperature of from 100° C. to 150° C. (212° F. to 302° F.) At a temperature of about 200° C. (392° F.) it again becomes brittle, and at 412° C. (773° F.), according to Daniel, the metal fuses, while at 1040° C. (1904° F., Deville and Troost) it boils. Zinc is hardened by rolling, and requires annealing at a *low* temperature to restore its malleability; but, if heated to a temperature near its melting point, the metal then becomes brittle whether slowly or rapidly cooled, in which state the metal, when bent, emits a sound resembling the "cry of tin," but somewhat more feeble. It is *volatile* at a bright red heat, the vapours taking fire in the atmosphere and burning with a bluish-white flame, with the production of a white powder of zincic oxide (ZnO); but it is not acted upon by exposure at the ordinary temperature to dry oxygen, though, if exposed to the atmosphere or moisture at the ordinary temperatures, its surface rapidly becomes coated with a layer or film of a grey oxide, which does not, however, increase by continued exposure, but protects the metal from further action. If carbonic anhydride be also present, the coating is more rapidly formed, and consists then of a basic carbonate of zinc. The specific gravity of cast-zinc is 6·862, which by pressure, as by forging, rolling, etc., is increased to 7·21; it contracts but slightly on solidification and cooling from the fused state, and this quality, together with the great

ease with which two pieces are soldered together, has led to its somewhat extensive use for the production of ornamental castings, which are in all cases cast in small pieces (although some of the ornaments are of considerable size), then soldered together, and the connections afterwards dressed off by the workmen—zinc expands $\frac{3}{16}$ th of its length by heating from 0° to 100°C. (32° to 212° F.) Pure zinc dissolves slowly in hydrochloric or sulphuric acid, while ordinary commercial zinc dissolves readily in these acids at the common temperature, with the liberation of hydrogen—the dark grey residue obtained on treating the commercial metal with these acids consisting chiefly of lead. Zinc is also dissolved by nitric acid and by digestion in aqueous solutions of the alkalies. It also reduces many metallic oxides if melted with them, while nearly all the metallic chlorides and fluorides are reduced when heated with the vapour of zinc in an atmosphere of hydrogen. When heated with nitre or potassic chlorate, then zincic oxide is produced, the action being accompanied by a violent deflagration. At a red heat, zinc decomposes the vapour of water readily; and at a very high temperature its vapour reduces carbonic anhydride (CO_2) to carbonic oxide (CO), while at a lower temperature zincic oxide is reduced by carbon or carbonic oxide—the latter constituting the active reducing agent in the extraction of the metal on the large scale. Silver, gold, platinum, bismuth, antimony, tin, mercury, lead, etc., are displaced from their solutions by zinc. The symbol of zinc is Zn , and its atomic weight is 65.

67. Impurities in Commercial Zinc.—*Arsenic* is a frequent impurity in English zinc, though much commercial zinc is free from this impurity.* *Bismuth, antimony, copper, silver, and tin* are not often found in the metal; while *iron* and *lead* constitute the most frequent impurities. The effect of tin or iron in the metal is to impair its malleability.

Iron ranks as the most important and most frequent impurity of zinc—its presence rendering the metal much harder, and causing it to become hot and crack during its rolling for zinc plates. Its presence is also indicated in the fracture of an ingot by its greyer appearance and the presence of a number of black specs on the faces of the cleavage planes, while the

* Eliot and Storer.

pure metal exhibits clear brilliant cleavage planes on fracture. The zinc may be freed from this impurity by redistillation, avoiding in this process all contact with iron.

Lead, introduced from the galena most frequently accompanying zinc blende, is almost always present in commercial zinc in amounts not exceeding 1·5 per cent., for although these two metals do not alloy well together, yet on melting them together, and then allowing to cool, the lead holding about 1·5 per cent. of zinc will separate and form the lowest stratum; while the zinc, with a like proportion of lead, forming a less dense alloy, occurs as an upper layer. In this manner the zinc intended for rolling is comparatively freed from lead, the pigs or ingots of zinc being melted upon the bed of a reverberatory furnace made to slope down to a deep cavity, well, or sump at the flue end of the hearth, and into which the metal flows as it melts—the temperature employed being insufficient to ignite the zinc. The metal separates in this well into two layers, the lowermost containing the lead, while the upper is zinc comparatively free from lead—the latter being ladled, through an opening at the end of the furnace, into ingots of a size convenient for rolling purposes. *Sulphur* is most generally present in small quantities in commercial zinc.

68. Zinc and Oxygen—Zinc, as already stated, if heated to a temperature a little above its melting point, takes fire and burns with a bluish-white flame, with the production of zincic oxide (ZnO), formerly known as *flowers of zinc*, *lana philosophica*, etc., which compound is yellow while hot, though white when cold. Zincic oxide also occurs native, as *zincite* or *red zinc ore*. Zincic oxide is reduced to the metallic state at a strong red heat by either *carbon*, *carbonic oxide*, *hydrogen*, or *iron*; and if heated with sulphur then zincic sulphide is formed with the evolution of sulphurous anhydride. Zincic oxide combines with silica in definite proportions with the production of difficultly fusible silicates, which are reducible by carbon (Percy); and with boracic acid this oxide yields readily fusible compounds. Zincic oxide constitutes the pigment known as *zinc-white*, used for the protection of iron from rust, and proposed as a substitute for white lead, since it is not blackened by exposure to sulphuretted hydrogen, but it lacks the body and opacity of the former,

This compound is prepared on the large scale by conveying the vapours of zinc, distilled from clay retorts, into chambers through which air is kept in circulation, when the metal burns, and the oxide, with more or less metallic zinc, is deposited in a series of condensing chambers.

69. Zinc and Sulphur.—These elements have not very powerful affinities for each other; but, by projecting a mixture of sulphur and finely divided zinc into a red-hot crucible, combination takes place with incandescence (Percy); but a considerable proportion of the zinc remains uncombined and merely mixed with the sulphide. Zincic sulphide (ZnS) also results when zinc turnings and cinnabar (HgS) are strongly heated, or when zincic sulphate is heated with sulphur or carbon; and, as an hydrate, it is precipitated from neutral or alkaline solutions of soluble salts of zinc as an amorphous white powder, when an alkaline sulphide, as ammonium sulphide, is added thereto. As prepared by the dry methods, zincic sulphide is a white or yellowish-white powder which is practically infusible (Percy), and tends to diminish the fusibility of other sulphides or reguli when combined with them; if roasted with access of air, sulphurous anhydride is evolved, and the residue contains zincic oxide and sulphate—the latter suffering decomposition at a full red heat, leaving a residue of zincic oxide. But this sulphide is a substance difficult to roast absolutely sweet, although it has but little tendency to clot, and thus permits of a somewhat high temperature being employed in the earliest stages of the roasting process. Zincic sulphide is decomposed when heated to redness with metallic iron, the zinc being volatilised while ferrous sulphide remains; similarly, carbon and steam effect the decomposition of zincic sulphide; and a mixture of zincic sulphide and oxide heated to a high temperature reduce one another after the manner of the corresponding copper compounds.* Zincic sulphide is readily oxidized by fusion with nitre or sodic nitrate. This compound occurs native in the ore known as "blende" or "black jack."

70. Zinc with Phosphorus.—These elements combine under the influence of heat, yielding a sublimate having a metallic lustre and vitreous fracture, while the presence of

* Percy, Vol. I.

small quantities of phosphorus diminishes the fusibility of zinc, and at the same time imparts to the metal a colour and lustre resembling that possessed by lead.

71. Zinc with Arsenic.—Union of these elements occurs readily without fusion, the application of a gentle heat sufficing to effect the combination, and, like phosphorus, its presence renders the fusion of the metal more difficult. The occurrence of arsenic in commercial zinc is noticed under the impurities of the metal.

72. Alloys of Zinc.—Zinc is of extensive application to the arts, as an element entering into the composition of a large and important series of alloys, to which, when present in certain proportions, it communicates a degree of hardness without impairing the malleability of the alloy; while in larger proportions it often induces brittleness in the product. Zinc also lowers the melting point of the metals with which it is alloyed, and renders them less alterable by exposure to the atmosphere; but owing to the low melting point and volatility of zinc, the preparation of its alloys requires considerable care to prevent unnecessary loss of the metal.

With *copper*, it forms the numerous varieties of brass, Muntz metal, etc., described at page 183; and with *tin* in addition, it constitutes the varieties of bronze, tombac, etc., already described.* Alloyed with from 40 to 60 parts of *copper* and 20 to 30 parts of *nickel*, it yields the different qualities of *German silver*.

Zinc and *lead* do not alloy well together; if the two metals be melted together and then left at rest, the alloy separates into two portions or layers, the upper one a plumbiferous zinc containing about 1·2 per cent. of lead (Mattheisen), and a lower or zinciferous lead containing about 1·6 per cent. of zinc.

With *mercury* zinc amalgamates readily, especially on the application of a very gentle heat; and, with the addition of *tin*, in the proportion of 50 parts of mercury, 25 of zinc and 25 of *tin*, it forms the *amalgam* employed for the rubbers of electrical machines.

Zinc alloys readily with *tin* upon fusion of the two metals,

* Vol. I., page 209.

the alloy being harder than tin but less ductile; it also readily alloys with *silver*, *gold*, *platinum*, and *palladium*, but the substances so produced are of little or no practical application to the arts.

Zinc also enters to the extent of about 1 per cent. into the composition of the English bronze coinage.

73. Ores of Zinc.—Zinc is said to have been found in Australia in the *native* state, but its chief forms of occurrence are the *carbonates*, *oxide*, *sulphide*, and *silicate* of the metal, which, though tolerably abundant in certain localities, are not widely diffused; and their occurrence in England cannot be considered as extensive, although ores of zinc occur in the limestones of Cornwall, Devonshire, Somersetshire, Derbyshire, and Cumberland, as also in Flintshire in Wales.

Calamine, or the native zincic carbonate, is, when pure, colourless or quite white with a pearly lustre, but owing to the presence of oxides of iron, etc., it usually occurs as a brown or buff coloured mineral, giving a white streak and an uneven or conchoidal fracture. It forms by far the most important and abundant ore of zinc. It is found in Belgium, Silesia, Carinthia, Westphalia, Poland, Hungary, Siberia, France, Spain, and the United States; occurring also in several counties of England, in the Lead-hills of Scotland, and in parts of Ireland. It contains, when pure, 52 per cent. of the metal, but it is usually accompanied by oxide of iron, carbonates of lime, magnesia, iron, and cadmium, along with baric sulphate and clay, and is often associated with blende (ZnS), galena (PbS), and the hydrated silicate of zinc, known as *electric calamine*. Calamine occurs in veins, beds, and pockets, usually traversing the limestones of Devonian, Carboniferous, or Oolitic age.

Red zinc ore, *zincite*, or oxide of zinc, occurs both amorphous and crystallised. This mineral in its pure state is quite white; but as occurring generally, it has a red colour, due to the presence of the oxides of manganese and iron, and more especially of the former, which thus imparts to the mineral its characteristic colour. This ore occurs largely in New Jersey in the United States, where it is raised and smelted, the oxide being here associated with willemite, franklinite, blende, etc., and the ore after treatment with anthracite dust

for the extraction of zinc, leaves a highly manganeseous residue, which is smelted in blast furnaces for the production of speigeleisen.

Blende, or zincic sulphide (ZnS), known to the miners also as "black jack," occurs both massive and crystalline. It has a vitreous lustre and conchoidal fracture; it varies in colour from white, to yellow, brown, greenish, and almost black; it is rarely free from sulphide of iron. Blende usually occurs as a highly lustrous, black, brownish-black, or yellowish mineral, sometimes possessing a reddish tint from admixture with galena (PbS); but the pure zincic sulphide is perfectly white, and like most other zinc ores, it is most frequently accompanied by cadmium, while iron and copper pyrites, with galena, are frequent associates of the mineral; it sometimes contains antimony in addition, and may be sufficiently argentiferous to render profitable the extraction of its silver. The pure zincic sulphide contains 67·03 per cent. of zinc; but blende contains on an average only from 45 to 60 per cent. of the metal. Blende is an abundant ore of zinc, occurring in the limestones and sandstones of Cornwall, Devonshire, Derbyshire, Wales, the Isle of Man, Perthshire, the Lead-hills, and some districts of Ireland; also in Hungary, Bohemia, Carinthia, the Hartz mountains, and other places on the Continent; likewise in New Jersey and the United States.

Electric calamine, or basic hydrated zincic silicate, occurs in tolerable abundance, associated with the ordinary calamine or zincic carbonate, with lead ores and with blende; but owing to the difficulty of its reduction it is not smelted in this country for the extraction of zinc, though it is worked in Hungary, Silesia, Poland, Spain, the Hartz, etc.

Willemite is an anhydrous zincic silicate, which occurs at Vieille Montagne in Belgium, at Stolberg in Carinthia, New Jersey, etc.

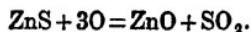
EXTRACTION OF ZINC FROM ITS ORES.

Zinc is always extracted by a process of distillation, the metal volatilising, as already noted, at a bright red heat, or about 926·5°C. (1900°F.); and when calamine or blende is the ore operated upon, the reduction is always effected from zincic oxide (ZnO), the *blende* undergoing a preliminary

roasting or calcination for the elimination of its sulphur; while *calamine* is not always roasted, since the carbonic anhydride (CO_2) is expelled by the heat of the furnace during the earlier stages of the distillatory process. Yet it is the usual practice to calcine calamine, since, after calcination, the ore is left less compact, and therefore more readily acted upon by the carbonaceous matters employed for its reduction, and at the same time the calcination expels moisture which would cool the retort, besides probably carrying off a proportion of zincic oxide mechanically suspended. The distillation is carried on either *per descensum*, as conducted in the English method of reduction, where the zinc vapour is drawn downwards from the bottom of the pot or crucible to the condensing apparatus; or *per ascensum* as practised in Silesia, etc., where the vapour of the metal passes out from the uppermost point of the crucible or retort to the condensing apparatus. The principal works for the extraction of zinc in England, are located at Swansea, Sheffield, Birmingham, Llanelli, Bristol, Wigan, and Wrexham.

74. English Process for the Extraction of Zinc.—If blende (ZnS) be the subject of operation, it is first picked as free as possible from galena (PbS), then stamped or crushed between iron rolls, and afterwards carefully washed to separate earthy matters. The ore thus prepared is roasted or calcined in a reverberatory furnace or calciner of some 10 ft. in length and 8 ft. in width, or in a furnace of which the bed is divided into three steps, on to which the ore is progressively raked from the flue to the bridge end of the furnace, in which case the total length of the bed attains to 35 or 40 ft., with a width of from 8 to 10 ft.; while a third variety of calciner consists of two beds, one above the other, the ore being first introduced on to the uppermost floor, the flame and products of combustion passing over the first floor, and then over the second before escaping by the stack; and the ore, after exposure for a certain length of time on the upper bed, is raked through an opening between the two on to the lower bed, where the calcination is completed. The flat bedded calciner first named operates upon charges of from 15 to 20 cwt. of blende, which is spread over the bed of the furnace and stirred at frequent intervals, the roasting

being continued for from 12 to 20 hours, during which time sulphurous anhydride continues to be evolved and zincic oxide remains, thus,



If calamine be the ore under treatment, it is either directly introduced into the distillatory apparatus, or it is first reduced to a coarse powder and subjected to a preliminary calcination by which water and carbonic anhydride are expelled, and the zincic oxide with earthy matters remaining, is obtained in a form readily reducible to powder.

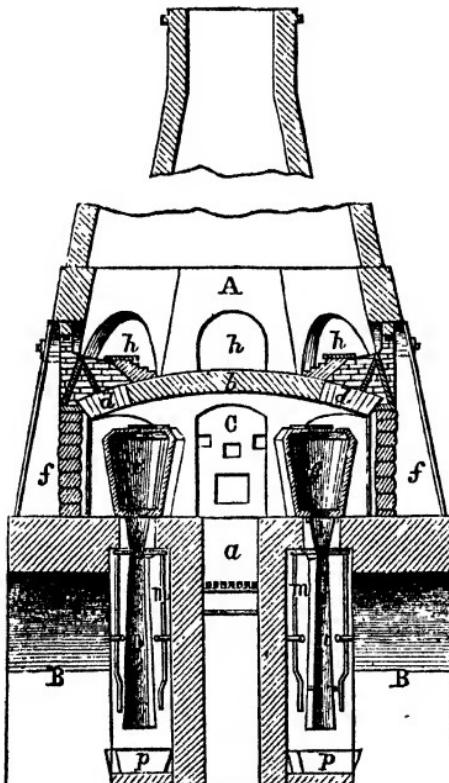


Fig. 36.—VERTICAL SECTION OF THE ENGLISH ZINC FURNACE.
The English furnace for the smelting of zinc is (including

the *cave*) about 40 feet in height, and has externally the form and appearance of the ordinary glass working furnace. It consists of a lower portion or *cave* B, fig. 36, octagonal in plan, and which contains the receivers and condensing apparatus. The roof of the *cave* forms the floor of the chamber C, in which are placed the pots, usually six in number, placed three upon each side of the fireplace *a*, which runs along the middle and across the furnace; the chamber C is closed by the low arch *b*, in which are openings *d d* for the introduction of the charge into each pot, and which openings also act as flues, whereby by inserting or withdrawing a slab or quarry, which can be placed over each, communication is opened or closed between the chamber C and the *dome* A, which surmounts the whole, and by these means a little back pressure can be maintained in C, so that in case of the walls cracking, the flame rushes out, and cold air does not obtain access to the pots, which are thus prevented from being cracked by this cause. The *dome* A acts as a chimney to the furnace, and also serves to better retain the heat of the furnace. The arched openings *ff*, which are bricked up with large pieces of brick during the working of the furnace, are for the introduction and withdrawal of the pots *ee*; and in the *dome* A are corresponding arched openings *hh*. The openings at the ends of the fireplace are not closed by a door, but are loosely stopped with coal piled up in the opening. The pots or crucibles *ee* are 4 feet in height, and 2 feet 6 inches in diameter, with an opening or mouth at the top for the introduction of the charge, which is afterwards closed by a loose cover, and the bottom of each pit is perforated with a hole to which is connected the condensing apparatus, consisting of the sheet-iron conical tubes *ll*, *nn*, supported by the rods *mm*, from eye-bolts in the side walls, whereby the flange on the top of the tube *l* is placed in contact with the bottom of the pot, so that the axis of the tube coincides with the centre of the hole in the bottom of the pot; while beneath the lower extremity of each of the condensing tubes is placed an iron dish or receiver *p*, into which the metal falls as it is distilled.

The crucibles or pots are made of Stourbridge fire-clay, old pots freed from vitreous matters, together with glass-house potsherds, the whole being reduced to powder, and kneaded

with water after the manner described for the manufacture of the crucibles for melting steel, except that the zinc pots are moulded wholly by hand in a wooden mould, with a special contrivance for obtaining the form given to the top of the crucible.

After the pots have been inserted in the furnace, the apertures *f*, *f* are bricked up, and the top piece *l* of the condensing apparatus is coated with clay, both on its inside and outside, and fixed in position against the bottom of the pots. If the furnace be cold, and the pots are all new ones, the whole is gradually heated so as to vitrify the surface of the pots (which have been sprinkled with river sand for that purpose), and so prevent their cracking during their working; but if the furnace is already heated, and a defective pot is required to be replaced by a new one, the fresh crucible is first heated to redness in a reverberatory furnace, and transferred while still hot by means of tongs to its position in the smelting furnace. The pots are then ready for charging, for which purpose the hole in the bottom of the crucible is first loosely stopped by introducing a few pieces of wood, which, carbonising, prevent the passage of the powdered ore down the pipes and so into the receiver, but are yet sufficiently permeable to allow the gases and vapour of zinc to pass downwards, or the same purpose may be accomplished by first introducing into the crucibles a few lumps of coke. On the stopping so introduced, the charge of 3 or $3\frac{1}{2}$ cwts. of calcined blende or calamine, or a mixture of the two, is introduced into each pot or crucible, along with about 2 cwt. of coke or anthracite, the ore and reducing agent being placed in alternate layers, it not being necessary to mix the ore and coke or coal before their introduction into the pots, since the reduction of the metal is not essentially effected by carbon, but by carbonic oxide. When the pots have been thus wholly charged, the lids or covers of the crucibles are luted on and the temperature gradually raised.

The vapours which *first* appear at the bottom of the short tube *l*, burn with a brown colour, from the combustion of cadmium, which very frequently accompanies zinc ores, and which, being more volatile than the zinc, distils over in the earlier stages of the process. This *brown blaze* is succeeded, as the temperature attains to whiteness, by the blue or bluish-white

flame of carbonic oxide containing vapours of metallic zinc, when the longer condensing tubes *n*, about 8 feet in length, are connected to the tube *l*, whereby the flame is extinguished and the zinc is condensed, and gradually falls down into the receiver placed beneath. When zinc ceases to be condensed, the residues remaining in the crucibles are withdrawn through the hole in the bottom of the pots, and the pots are then ready for recharging. If a condensing tube becomes stopped by the condensation of the metal and deposition of zincic oxide within it, the obstruction is at once removed by detaching the pipe *n*, and inserting a red-hot iron into the tube to melt the solidified zinc, which then falls down into the receiver; while occasionally an explosion occurs in the cave or vault from the ignition of the mixture of oxygen and carbonic oxide in the condensing tubes.

A furnace of the capacity above described will work off about 5 tons of ore per fortnight, yielding in the same time about 40 cwt. of zinc, and the crucibles will last about four months before requiring renewal; but it will be necessary in the interval to plaster over cracks or leakages with fire-clay, introduced through apertures in the openings *ff*, without the necessity of removing the pots from the furnace.

The English method of extracting zinc entails a very small expenditure of manual labour, but it involves a much larger consumption of fuel than is required in the Belgian or Silesian processes, to be subsequently described, and also any electric calamine accompanying the zinc ore entirely escapes reduction; for these reasons this method of smelting zinc has been almost entirely superseded by the Belgian method of reduction.

Carbonic oxide is always produced in the reduction of zinc, thus,



attended perhaps by a small quantity of carbonic anhydride (CO_2); since, whether carbon or carbonic oxide forms the active reducing agent in the preparation of this metal, the high temperature required for the reduction is sufficient to immediately convert into carbonic oxide, by contact with the excess of carbonaceous matters always present in the crucible, any carbonic anhydride that might be first formed.

The zinc, as obtained above, is known as "*rough zinc*," for, as collected in the receiver, it does not form a solid cake, but consists of a non-homogeneous mass of metal, enclosing zincic oxide and other mechanical impurities between its particles, and for the separation of which the rough zinc is melted, formerly in cast-iron pots, but latterly clay vessels have been substituted, since zinc melted in contact with iron takes up a proportion of the latter, and the quality of the zinc, especially for rolling, is thereby impaired. These melting pots are each heated by their own fire placed beneath the pot, and the molten metal is well stirred, when the oxide with the impurities rise to the surface and form a scum, which is skimmed off, and constitutes what is known as "*sweeps*," the sweeps being returned to the smelting crucibles at the next charge. After this treatment the surface of the zinc is left clean, and the metal is ladled into open moulds forming *cakes* or *ingots*, as required for commerce.

75. Belgian Method of Extraction.—This method, now largely carried out in England and elsewhere, is adopted at the Vieille Montagne Company's works in Belgium, and is the method by which about one-fourth of the zinc occurring in commerce is prepared. The ores adapted to this process are the carbonates, silicates, and oxides of zinc, or a mixture of these is more usually employed, the ore before smelting being roasted or calcined—a process conducted at the Vieille Montagne Company's works in open-topped kilns, from which the products of the calcination are withdrawn through openings in the sides of the kiln which are connected with a suitable flue; but the small ore is usually calcined in reverberatory furnaces.

The calcined ore is then ground to powder, and mixed with half its weight of *small coal* or *carbonaceous matters*, and the mixture of ore and reducing agent so obtained is (after slightly moistening to prevent its blowing away) introduced by a suitable ladle into the series of cylindrical fire-clay retorts *a*, figs. 37 and 38, which are closed at one end, and arranged with their open extremities or mouths to the front, in an arched vertical chamber well braced together by iron standards and tie-rods, each furnace or chamber containing from sixty to eighty of these retorts, arranged in eight tiers

of from eight to ten in a tier. The retorts are from 39 to 42 inches in length, and from 6 to 8 inches in external diameter, and their posterior or closed extremities rest upon notches built in the back wall of the furnace, while ledges of

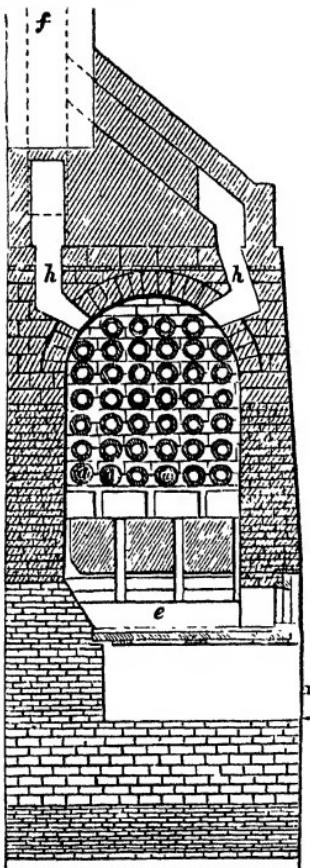


Fig. 37.—LONGITUDINAL VERTICAL SECTION OF BELGIAN ZINC FURNACE.

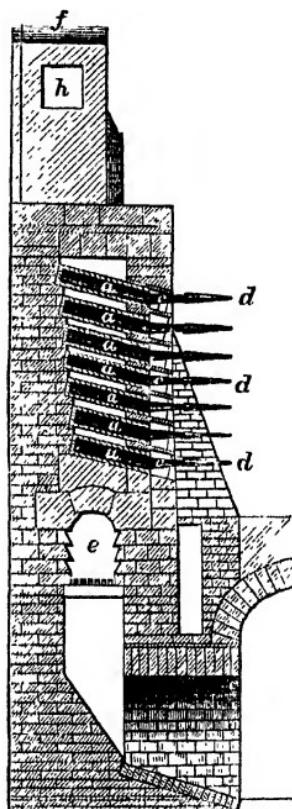


Fig. 38.—TRANSVERSE VERTICAL SECTION OF BELGIAN ZINC FURNACE.

cast-iron are arranged in the front of the chamber for the support of the front ends of the retorts, the rear ends being supported as shown, at a higher level than are the front, so that the retorts incline downwards from the back to the front;

while to the mouth of each retort is luted a simple bellied fire-clay nozzle or condenser *c*, about 12 inches in length, to the front extremity of which is again fitted a more conical iron tube *d*, which latter serves to condense and collect the "fume" or crude zincic oxide (ZnO) which passes over along with the zinc during the distillation, and which is detached by the workman from these nozzles or receivers at intervals of about two hours, and is returned to the retorts with a subsequent charge. The fireplace (*e*) is situate beneath the lowest row of retorts, while coal is the fuel employed, and the products of combustion pass through openings in the roof of the fireplace, then around and between the various retorts, before escaping by the two flues *h h* from the top of the retort chamber to the stack *f*; four such furnaces being usually arranged in a group with the stack between them, the latter being divided by partitions into as many compartments or flues as there are furnaces in the group, so that each furnace can be controlled by its own damper.

It is obvious from the arrangement of the furnace, that the retorts will not be equally heated, but that the temperature of distillation will decrease from the lower to the upper tiers of retorts; and to maintain a regularity of the process in different parts of the furnace, the retorts in the lower tiers are charged more heavily than those in the upper rows; thus, while the lowest retorts receive a charge of 28 lbs. of ore and reducing agent, those in the upper rows receive but 16 lbs. of the mixture; also, the less refractory materials as "zinc fume" from the nozzles, etc., and ores containing much oxide of iron, are introduced into the upper retorts, since the latter class of ore would give rise to the production of a fusible ferrous silicate at the temperature attained in the lower retorts; while the more refractory zinc ores are also introduced into the lower tiers, and the lowest tier of all is occupied by empty retorts, somewhat thicker than those to be charged, which thus serve to protect those of the next row from the intense local heat immediately over the fire.

In introducing new retorts into the furnace, the retort-chamber is first raised to a high temperature, and then the retorts, also previously heated to redness in a separate furnace, are introduced and fixed in their places, when the

nozzles (*e*) are connected to the retorts, and the charge of ore and coal introduced by a suitable scoop through the nozzle into the retort, when, after a short time, the blue flame of carbonic oxide is observed burning from the mouth of *c*; but after a further short interval the transparent flame becomes more opaque, luminous, and of a greenish-white colour, due to an admixture of burning zinc, with the escaping carbonic oxide, and at this stage the conical sheet-iron pipe (*d*) is attached, when the distillation proceeds as described, the greater part of the zinc condensing in the hollow or belly of the nozzle *c*, from which it is ladled or raked out at intervals of about two hours, in quantities of a pound or two at once.

The process thus involves a considerable expenditure of manual labour, while its consumption of fuel is only from 5 to 6 tons of coal per ton of zinc produced, which is little more than one-half the amount required in the Silesian process, and about one-fourth of that used in the old English process; but the residue left in the retorts on the completion of the distillation retains about 10 per cent. of zinc, in combination with silica derived from the clay retorts, and from which the zinc cannot be separated by this process, but is lost from the difficulty attending the reduction of zincic silicate.

The charge being worked off, the residues are raked well out into a pit in front of the furnace, and recharging immediately commences, two charges being worked off during the twenty-four hours; and the furnaces are thus worked continuously, until requiring to be stopped for repairs, which, on an average, will occur at intervals of about two months.

The *rough* metal obtained by this method of distillation requires, before it is ready for the market, to be remelted for the separation of the zincic oxide, etc., with which it is accompanied, and which rises to the surface on remelting, forming a scum which is removed as long as it forms; after which the metal is cast into ingots, weighing from 70 lbs. to 80 lbs. each, in which form it is sent into commerce.

At the works of the Vieille Montagne Company the ore is first washed for the separation of clay, etc., which accompanies the calamine more or less, after which it is calcined in the manner already described, the ore losing by this treat-

ment about 25 per cent. of its weight, and it is then treated in the Belgian furnace in the manner just described.

76. Silesian Method of Extraction.—The chief difference between this and the Belgian method last described, exists in the construction of the furnace and retorts; for in the Silesian process the retorts are supported throughout their whole length, and a greater heat may be thereby attained without fear of the retorts collapsing than is permissible in the Belgian process, thus rendering it practicable to smelt poorer ores by the Silesian process than can be profitably employed for treatment by the previous methods; while the residues left in the retorts, instead of containing some 10 per cent. of zinc, as in the Belgian process, do not retain more than perhaps 5 per cent. or 6 per cent. of metal. In consumption of fuel and expenditure of manual labour, the process stands intermediate between the Belgian and old English methods of reduction; and by the application of the Siemens' regenerative furnace to the process, the consumption of fuel has been somewhat further reduced.

The ores employed in the Silesian process are, as before, chiefly oxides, carbonates, or sulphides of zinc, which may be profitably smelted if they contain not less than about 20 per cent. of metal. The ore is first calcined as thoroughly as possible in a reverberatory furnace having two tiers or floors one above the other, or with a single bed divided by a step into two portions; the ore being first roasted for about twelve hours on the bed having the lowest temperature, when it is exposed for a like period to the higher temperature of the other portion of the bed, the furnaces being heated either by their own fire or by the waste gases from the smelting furnace, and the ore loses during calcination about 2 per cent. of zinc.

The calcined ore is broken up into small pieces, and mixed with about one-tenth of its weight of "sweep," and one-half of its weight of carbonaceous matter, as coal or coke, the mixture being then introduced into the series of \square -shaped retorts or *muffles* (*a a*, fig. 39), measuring about 3 feet in length, by 1 foot 6 inches in height, and 8 inches in width, and each weighing, when dry, about 200 lbs. The retorts which are made of a mixture of Stourbridge or other good fire-clay,

mixed with the powder of old pots or muffles freed from slag and vitreous matters, are formed by hand after the manner described for the preparation of the Belgian retorts, and like them require careful annealing before use. Near the upper extremity of the front end of each muffle is attached the curved clay condensing tube *b*, at the angle or bend of which is placed the movable plate *c*, capable of removal for an examination of the interior of the muffle and the introduction of the charge of ore and carbonaceous matters; while, at the same end of the muffle, beneath the condensing tube, is sometimes placed a second opening for withdrawing the residues, etc., left in the retorts at the completion of the distillation, and which is luted up during the conduct of the process. To the end of *b* is attached a cast-iron tube, at the extremity of which is a sheet-iron prolongation, which conveys the metal and products of distillation to a chamber (*f*) below the level of the bottom, and in front of, the retorts, where the zinc is collected as it condenses. From 20 to 28 of these muffles are usually arranged,

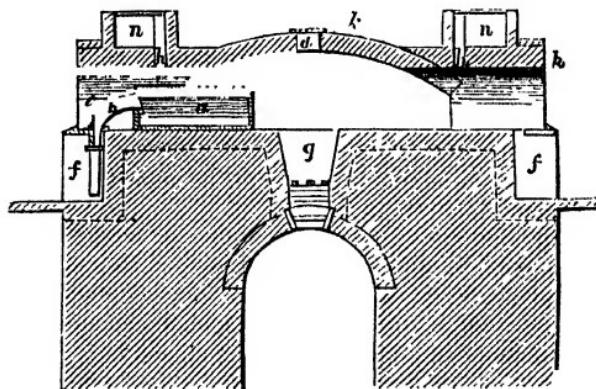


Fig. 39.—SECTION THROUGH ONE OF THE MUFFLES IN THE SILESIAN ZINC FURNACE.

as shown in fig. 39, in two rows, back to back, in a rectangular and nearly square furnace, the muffles resting upon platforms of brickwork built along the sides of a central fire-grate, and sloping slightly from the fire towards the front end of the muffles; and the fireplace does not pass quite through

the furnace, but is stopped at some distance from the back. The sides or faces of the furnace are divided by vertical bricks or tiles, on which abut small arches, into a number of equal rectangular and arched compartments, each holding a pair of muffles; and the closed extremities of the muffles are placed nearest the fire. In the arch *k*, enclosing the furnace chamber, is an opening (*l*) from each compartment or pair of muffles, which communicates with one of the two flues (*nn*) running along the top of the furnace, and which lead to the stack at the back of the furnace; or, instead of these openings and flues on the top of the furnace, the gases and flame from the fire, after circulating around the muffles, are withdrawn in the later Silesian furnaces through openings in the brick-work, on which the muffles rest, downwards into flues below, instead of above, as indicated in the figure; which latter arrangement has the advantage of heating the muffles beneath, as well as above—whilst, in the former method, the heat is applied wholly from the top sides of the muffles. In the arch or roof of the furnace (*k*) also are openings, closed by movable tiles, through which the workmen obtain access with mops and fire-clay lute, to lute up any cracks that may occur in the retorts during the working off of a charge. The front of the chambers or recesses in which the retorts are placed are closed during the working of the furnace by sheet-iron doors, each provided with a peep-hole for observing the temperature of the furnace.

The charge for each retort or muffle averages about 103 lbs., made up of 65 lbs. of calcined ore, 6 lbs. of sweep or skimmings of crude zincic oxide from the remeltings, 23 lbs. of finely-powdered bituminous coal, and 9 lbs. of coke; but the muffles near the front end of the furnace being subjected to a higher temperature than those in the rear, they are made to receive a proportionately larger weight of materials, so that the whole of the retorts may work off their charge in the same time, which, including the cleaning out of the muffles and their preparation for receiving the succeeding charge, occupies about 24 hours; while a retort will last from 8 to 12 weeks, according to the part of the furnace in which it is situate, before requiring to be replaced by a new one.

When the retorts are all charged, the temperature is gradually raised, the first effect of which is the expulsion of a little moisture; this is succeeded as the heat increases by carbonic oxide (CO) and a little zincic oxide (ZnO), accompanied by some finely-divided zinc; when, after about 5 hours, the temperature having gradually increased, the blue flame of carbonic oxide burning at the nozzle of the condensing tube becomes more luminous and greenish-white in colour, as described in the previous methods—which appearance is succeeded, after a short interval, as the temperature continues to rise and attains to whiteness, by drops of the metal condensed in the nozzles; after which the distillation, if properly conducted, goes on uninterruptedly for about 12 hours, when the operation will be completed.

Instead of the elbow-shaped condensers, with their iron appendages as described above, some Silesian furnaces, as at Stolberg, etc., have been fitted with condensing apparatus after the manner of the Belgian condensers, consisting of a clay nozzle some 2 feet in length, egg-shaped in vertical section, and in which is a depression or belly in the middle of its length; and in the lowest point of which is a hole from which the metal can be drawn off at intervals as the cavity fills; or, in the absence of the hole, the metal can be ladled out through the mouth as the cavity fills with the condensed metal.

77. Carinthian Method of Reduction.—In this process, as formerly carried on in Carinthia and Hungary, the distillation is "*per descensum*,"—the furnace consisting of an arched chamber, in which a large number of conical clay tubes or retorts are placed vertically, and with their widest end upwards; while at their lower ends they are fitted with collars which fit against each other, and so form a closed bottom to the furnace, supported upon a trellis-work of iron bars, below which is the condensing apparatus. The bottom of each of these tubes is first stopped with small pieces of charcoal, on which is introduced the charge, consisting of calcined calamine or roasted blonde, with powdered charcoal and lime, mixed together with a solution of wood ashes and common salt—the charge filling each tube to within 4 inches of the top, which space is filled with charcoal, the upper pieces being washed with a clay lute for closing the

top. The furnace is heated by the flame from a fire fed with wood, and the charge is worked off in from 30 to 40 hours; but a large loss of fuel is entailed from the necessity of cooling down the furnace before recharging after each charge is worked off.

78. Treatment of Zinc Fume.—As already indicated there collects in the flues, passages, and condensing apparatus employed in the distillation of zinc, considerable quantities of a grey *dust* or condensed *fume*, containing zincic oxide (ZnO), with finely-divided metallic zinc, along with arsenic and cadmium, which latter, being more volatile than the zinc, pass over and are condensed, especially in the earlier stages of the process. Frequently, also, lead and iron occur as constituents of the fume, along with alumina (Al_2O_3), lime (CaO), carbonaceous matters in large proportion, and sulphuric acid in smaller proportions.

This fume is either added to the smelting materials and returned at once to the distillatory apparatus, or, as at Bleiberg and elsewhere, the fume is first treated in what is known as the "*Montefiori furnace*" for the separation of any zinc that exists in the metallic state, and the residue, after this treatment, being alone returned as a constituent of the smelting charge of the ordinary zinc furnace. The Montefiori furnaces consist of a series of vertical cylinders or tubes of fire-clay, each about 8 inches in diameter and closed at one end; these are placed vertically, with their open ends or mouths upwards, on the two sides of a vertical wall within a rectangular chamber heated by a fire placed beneath the level of the platform supporting the cylinders, while the flame and products of combustion obtain access to the chamber through apertures in the arched roof of the fireplace. To the bottom of each cylinder is attached a tube at right angles to the length of the cylinders, which tube is bell-mouthed inwards, and opens beyond the outer walls of the chamber; and when the pots or cylinders are charged with fume, a clay stopper or piston, fitting the cylinder, and connected with an iron bar passing through an opening in the flat roof of the furnace, is placed upon the contents of each cylinder; so that by this means the fume is heated to the melting point of zinc without access of air, while pressure can

be applied as required to the top of the piston, whereby the particles of metallic zinc are melted and collected in the bottom of the pot, from whence it can be withdrawn by extracting a clay stopper placed in the lateral tube previously mentioned. But the metal so obtained is still very impure, from the presence of arsenic, cadmium, etc.

79. Separation of Lead from Zinc.—Ores of lead in larger or smaller quantity, frequently accompany zinc ores, especially as plumbic carbonate in calamine, or as galena (PbS) in blende (ZnS), while the zinc produced from such ores not unusually contains considerable proportions of lead, which it is desirable to separate as perfectly as possible from the zinc intended for rolling into sheets, etc.; and for this purpose, the plumbiferous zinc is subjected to a species of liquation, in which the pigs of zinc are heated on the sloping bed of a reverberatory furnace to a temperature below that at which the zinc will ignite, when, as the pigs melt and run down into the well or *sump* prepared at one end of the furnace bed, the lead, in virtue of its superior specific gravity, collects in the bottom of the well, while the zinc, largely freed from lead, forms an upper layer from which the metal is ladled and cast into ingots as it collects.

80. Sheet-Zinc.—Much of the zinc of commerce is employed in the form of sheets, and for their manufacture the pigs of zinc, as prepared at the smelting establishments, require to be remelted in a reverberatory furnace, in the hearth of which is a cavity into which the melted zinc drains, and from which it is ladled into moulds of a size and form convenient for rolling into sheets. These slabs are then heated to about 212°F . (100°C .) or a little beyond, and are rolled in the rolling mill to the thickness required.

81. Galvanised Iron.—The commercial article known under this name is an iron plate coated superficially with zinc; the iron, as already noted, giving rigidity and strength to the plate, while the zinc prevents the corrosion or *rusting* that occurs on the exposure of sheet-iron to atmospheric influences; but owing to the great ease with which zinc is attacked by acids, galvanised iron is not adapted as a constructive material where it would be exposed to acid vapours. In addition to plates, the process of galvanising is applied to

chains, links, and other articles requiring to be protected from corrosion; the coating of zinc being also rendered more firmly adherent if the articles of iron be first coated with a layer of tin after the usual manner of tinning.

The coating of zinc was originally deposited upon the surface of the iron by galvanic agency, and hence the name; but this method has given place to the more simple method of coating the cleaned surface of iron by simple immersion in a bath of melted zinc, the surface of the latter being kept covered with sal-ammoniac (NH_4Cl) in order to prevent oxidation, and at the same time to dissolve any zincic oxide that may be formed; and by this treatment the plate is covered with a thin, firmly adherent coating of metallic zinc, while a definite alloy of zinc and iron probably exists along the line of junction of the two metals. The bath of zinc in which the operation is performed becomes gradually impure from the presence of iron, small proportions of which are dissolved by molten zinc, and its effect is to render the metal less fusible, brittle, and hard. The ferriferous alloy collects in pasty masses at the bottom of the bath as the proportion of iron increases, and it may be largely separated by the use of a perforated ladle. The ferriferous zinc thus separated is less lustrous than the pure metal, presents a somewhat scaly aspect on fracture, and exhibits numbers of grey or black spots throughout its fractured surface. The zinc is in a great measure recovered from this alloy by a special distillation.

Galvanising of the iron wire, such as is employed for fencing, signal wires, etc., is performed with great rapidity, the rolled wire being annealed at the same operation; and for this purpose the rolled wire is drawn through a furnace of sufficient length, that the wire in its passage through it is heated to redness, while the heated wire, as it passes out from the furnace, is directed by guide pulleys through a reservoir of dilute sulphuric acid (pickle), which has the effect of clearing off any scale, and on leaving the pickle it passes through a quantity of sand, whereby the wire is obtained with a clean metallic surface for the action of the bath of metallic zinc into which the wire is next introduced. In this manner, while one end of the iron wire is still passing through the furnace for annealing, the other extremity is at

the same time being wound on to a drum in its galvanised or zinc-coated state.

ALLOYS OF ZINC AND COPPER.

Copper, when alloyed with zinc in various proportions, gives rise to a large number of important bodies, which are of extensive application in the arts; but of these the most important are *brass* and *Muntz's metal*. Other alloys, formed by the union of these metals, are *Tombac*, consisting of 84 parts of copper with 16 of zinc; *Pinchbeck* (3 parts of copper to 1 of zinc); *Princes' metal* (5 parts of copper to 1 of zinc); *Mannheim gold*, only another variety of Pinchbeck; *Bath metal* contains copper, and about 22 per cent. of zinc; but the exact composition of these latter alloys is exceedingly various, and the different names are applied by various authors to alloys having the same composition.

The alloys of copper and zinc range in colour between copper-red, reddish-yellow, yellow, and bluish or greyish-white, according to the proportion of zinc contained in the alloy, paleness of tint attending an increase in the proportion of zinc employed. They are homogeneous, generally brittle at a red heat, and require more frequent annealing while being hammered or rolled into sheets, etc., than does pure copper; while an excess of zinc in the alloys renders them brittle at all temperatures, and with the increase in its proportion the melting point and specific gravity of the alloy are lowered, thus a brass containing 25 per cent. of zinc melts at 954.4°C . (1750°F .). *Aich's, sterro, and Gedge's metal* are varieties of brass containing, in addition to copper and zinc, small proportions of iron, while *sterro-metal* contains tin in addition.

82. Brass.—This name is applied to most yellow alloys of copper and zinc, but *ordinary brass* is an alloy consisting of 2 parts of copper with 1 part of zinc, when it is almost golden-yellow in colour, is *harder* than copper, and accordingly resists wear better, is very malleable and ductile, any proportion between 50 and 37 per cent. of zinc alloyed with copper affording a brass which is sufficiently malleable to roll into good sheets; but the metal is hardened by hammering or rolling, and requires to be frequently annealed during these

processes to prevent its cracking at the edges; it can be drawn out into very fine wire, but at a red heat it is very brittle. The fractured surface of an ingot broken while hot is coarsely fibrous, while if broken cold the same ingot exhibits a finely granular fracture. Brass is rapidly tarnished by exposure to atmospheric influences, though it is not so readily tarnished and blackened as copper, and, by continued exposure to vibration, a crystalline structure is induced in the alloy whereby considerable brittleness results. It may be readily stamped or cast into a variety of ornamental forms; it has also an extensive application for castings used by the engineer, etc., since it yields a much more close and compact casting than copper, and thus forms a material resisting wear much better than the latter. Ornaments made of brass are capable of receiving a rich dead yellow surface by treatment with dilute nitric acid, the immersed article being allowed to remain in the acid (*dipping liquid*) until the adherent scale is readily rubbed off, when the brass, after washing with water, is then introduced into nitric acid a little stronger than the last, and in which it remains until the surface presents a white or creamy appearance, from the presence of adherent bubbles of gas; after again washing in water and roughly drying in sawdust, the articles are immersed for a few seconds in strong nitric acid, after which they are washed in water containing a little *cream of tartar* or *argol*, and are finally dried in hot sawdust.

The addition of about 2 per cent. of *lead* is made to brass intended for rolling, filing, or working in the lathe, but its tenacity or adaptability for wire-drawing is diminished thereby; while for engraving purposes its hardness is increased by the addition of a small proportion of *tin*. Iron is objectionable in brass, since it increases the hardness and impairs the lustre, tenacity, and malleability of the alloy. The alloy known as "*Dutch metal*" is a variety of brass containing a larger proportion of copper than the ordinary alloy, and which is capable of being hammered into leaf of less than $\frac{1}{50,000}$ th of an inch in thickness, in which form it is employed instead of gold leaf for the gilding of cheap articles. A common variety of brass contains equal parts of its two constituents, copper and zinc.

83. Calamine Brass.—The variety of brass known as “*calamine brass*,” since “*calamine*” (zincic carbonate) was employed in its production, instead of metallic zinc as now generally adopted, was for a long time looked upon as a superior variety of the alloy, and the process of “*cementation*” by which it was produced constituted the only method employed for the manufacture of brass; but at the present time few, if any, furnaces now occur in England in which calamine brass is produced.

The furnace employed in the preparation of calamine brass consists of a circular fire-brick chamber, contracted at the top to about one-third of the greatest diameter of the furnace; while the bottom of the furnace is formed of a cast-iron plate with 12 circular holes arranged symmetrically around a central and somewhat larger hole, the latter serving to rake out the ashes and clinker into the ash-pit below. To each of the smaller holes is applied a cast-iron conical tube or twyer about 6 inches in height, and the space between these several cones is then filled up to the level of their upper edges with fire-brick and fire-clay. The floor thus prepared constitutes the furnace bottom upon which are placed the *pots* or *crucibles* in which the charge is melted, the conical tuyers above mentioned serving as air-holes for the introduction of air from without to the interior of the chamber for the combustion of the fuel in the furnace, while the circular aperture in the top serves as the chimney for the furnace, and is kept more or less closed, as required during the operation, by a movable plate or tile placed above it. Several of these furnaces are usually built together, and over such a group is raised a chamber or dome of brickwork resembling the ordinary glass furnace.

The crucibles in which the brass is melted are arranged concentrically around a central or *king-pot*, the latter being sometimes larger than the rest, and capable of holding about 120 lbs. of metal, while the other pots only hold about 84 lbs. each.

The mixture with which the pots are charged consists of 100 lbs. of *calamine* or *blende*, previously ground fine and calcined *sweet*, together with 40 lbs. of ground coal; which ingredients, upon intimate mixture, are passed through a sieve of 8 holes to the inch, after which it is damped and

passed through a sieve of only 4 holes to the inch, when it is finally mixed with about 66 lbs. of *bean-shot* copper, and is ready for charging into the crucibles.

The crucibles, already at a red heat from a previous operation, are lightly charged with the above mixture, the mouths of the crucibles being then closed by placing across them large pieces of coal, while the smaller pieces of fuel are put around and between the sides of the several pots, care being taken to keep the air-holes in the bottom of the furnace well open. The cover is now placed partially over the mouth of the furnace, when the coal undergoes, during the first stage, a process of coking, upon the completion of which the cover is placed further over the furnace mouth for a short time. The heat is now gradually raised by a proper regulation of the draught, effected by withdrawing the cover as required from the mouth of the furnace, and, in about ten hours, the zinc will have been reduced from the calamine and alloyed with the copper, upon which the pots and their contents are ready for withdrawal. For this purpose the central or king-pot is usually first taken out, after which the side pots are successively withdrawn, and the contents of each, after well stirring with an iron rod, are emptied into the king-pot, and the crucible at once reinserted into the furnace for a repetition of the process, which thus goes on continuously as long as required. The brass is thus collected in the king-pot, which is then skimmed to clear it from dross, etc., and the metal poured therefrom into moulds suitable for the purposes to which it is to be applied.

84. Direct Preparation of Brass.—This method is either conducted in black-lead crucibles, heated in small furnaces similar to the steel-melting furnaces, F, page 162, Vol. I., or the metals are melted upon the hearth of a reverberatory furnace; the latter method being applied more especially to the preparation of the various yellow metals, employed as sheathing, etc., and the manner of its conduct is described in the ensuing article upon Muntz's metal.

In the direct preparation of brass, the copper is first introduced into the crucible and carefully melted, keeping the heat only just sufficient to maintain the copper in a state of fusion; and, when in this condition, the required proportion

of zinc, after allowing for the loss which always occurs from volatilization, is cautiously added to the molten copper. But since it generally occurs in practice that it is desirable to utilise a proportion of old brass, this latter, to the extent of about one-third the charge, is first introduced into the crucibles, and upon this is placed alternate layers of zinc, copper, and powdered charcoal, always completing the charge with a layer of the latter, for the charcoal serves to reduce any oxide that may be formed by oxidation during the melting. The furnace is then supplied with coke, and in about four hours the charge will be melted and the alloy ready for casting; and for this purpose the metal is skimmed and then poured into the required moulds: if for slabs intended for rolling, the moulds are of cast-iron, and are previously warmed, and the surface dusted over with charcoal; while sand moulds are employed in the production of brass castings, such as are required by the engineer, etc. When brass is ready and at a suitable temperature for pouring, its surface, on withdrawing from the furnace, emits a bluish-white lambent flame, due to the slight waste of zinc going on at the surface of the alloy at this temperature; and the quality of brass castings depends much upon the temperature at which they are cast.

85. Muntz's Metal.—This is a variety of brass which presents a finely granular fracture, and admits of being rolled at a red heat; it is extensively applied to the sheathing of ships, etc., since it is said to keep a cleaner surface than copper sheathing. Muntz's metal or yellow sheathing is described in the original specification as consisting of three parts of copper to two of zinc, and thus differs from ordinary brass in containing a larger proportion of zinc, while it is now the usual practice to add about one per cent. of lead to the alloy; and the nails or bolts employed in fastening it down are made a little harder by the addition of *tin*, such bolts having, according to Dr. Percy, a composition consisting of 86·82 per cent. of copper, with 3·88 per cent. of zinc, and 9·30 per cent. of tin.

The preparation of Muntz's metal may be conducted in the ordinary crucibles employed in brassfounding; but it is now more generally made in reverberatory furnaces, the copper

being first introduced and melted, when the required amount of zinc is gradually added, and the two metals thoroughly incorporated. When the requisite amount of zinc is supposed to have been added, test or trial samples (proofs) are taken from the furnace and hammered or rolled while hot, and afterwards broken, in order to judge of the condition of the metal from the appearance of its fracture; and from the appearance of this trial specimen more zinc is added, as may be required, until the trial piece indicates the proper condition, when the alloy is tapped out into a ladle lined with clay, from which it is laded into suitable ingot moulds.

The exact proportion of zinc cannot be at once added to the charge, since the loss by volatilization is considerable, and also very variable, and hence the necessity of determining the condition of the metal by actual trial pieces taken from the bath; while this uncertainty is further increased by the addition to the charge of old sheathing and yellow metal, which likewise loses a proportion of its zinc during the fusion.

In the neighbourhood of Swansea, etc., yellow or Muntz's metal is manufactured by melting the copper on the bed of a reverberatory furnace, while the zinc is melted separately in a small kettle at the end of the furnace, heated by the waste heat from the furnace; and when both metals are ready for mixture, the zinc is laded into a receptacle in front of the furnace, into which the copper is then tapped, the incorporation and alloying of the two being attended with an abundant escape of white fumes of zincic oxide with a consequent loss of zinc, which loss is stated, however, to be less than when the mixture is effected by introducing both metals into the furnace.

Sheets of Muntz's metal are annealed after rolling, and then immersed in a pickle of dilute sulphuric acid for the removal of the scale and oxide of copper thus formed, after which they are scoured with sand, and then washed and dried before packing for the market.

CHAPTER IV.

MERCURY.

86. **Physical and Chemical Properties.**—This metal, known also as *quicksilver*, has an almost silver-white colour, is tasteless and inodorous when pure, possesses a strong metallic lustre, and constitutes the only metal which, at ordinary temperatures, exists in the liquid state; but unlike ordinary liquids, it runs off without wetting ordinary non-metallic surfaces, while with many metallic surfaces the mercury unites with the metal, and deposits a film of an amalgam upon it. At a temperature of $-39\cdot44^{\circ}\text{C}$. (Hutchins), it solidifies with considerable contraction in volume, to a tin-white, ductile, and malleable mass, that may be beaten out with the hammer, cut by the knife, and even welded, while its fracture under these conditions is distinctly granular in appearance; and at a temperature variously estimated at between 346°C . and 360°C . ($654\cdot4^{\circ}\text{F}$. and 680°F .), the metal boils and assumes the form of a colourless vapour; various experiments have also shown that the metal is more or less volatile, either in air or vacuo, at all ordinary temperatures. The density of mercury varies much with the temperature, owing to its high co-efficient of expansion for heat; while the regularity of this expansion for equal increments of heat between certain limits, as from 0°C . to 100°C . (32°F . to 212°F .), renders it peculiarly well fitted for the construction of thermometers or instruments for registering the sensible heat of bodies, the increment of its expansion for each degree Fahrenheit corresponding to $\cdot00011$ (Dalton) of its bulk at 32°F .; the density of the metal at 4°C . is given by Regnault as $13\cdot596$, and the density of mercury vapour referred to air as unity is $6\cdot7$ (Brineau), though theoretically its vapour density would be $6\cdot933$. The specific heat of this metal is $\cdot03332$ in

the liquid state, or .03192 when in the solid state. Mercury is unaffected by exposure to air, oxygen, hydrogen, nitrogen, nitrous or nitric oxide, carbonic anhydride, or alcohol, and the first-mentioned thus forms a ready method of detecting any considerable amount of impurities in the commercial metal, since, on briskly shaking a quantity of mercury in a flask of air or oxygen, the baser metals are oxidized and form a grey pellicle upon the surface of the mercury, or if present in considerable proportion the oxides mixing with the metal reduce the whole to a grey pulverulent mass. By agitating or rubbing mercury with water, ether, sugar, or fatty matters, the metal loses its metallic lustre and appearance, or is *deadened*, and the whole is converted into a grey mass, or powder, of minute globules of mercury, between which are interposed strata or films of the fatty or other matters, so as to obscure from the eye the metallic character of the mercury mixed in the mass. If mercury be maintained in contact with the atmosphere at a temperature just above its boiling point, the metal is slowly oxidized to mercuric oxide. Mercury also readily combines with *gold*, *silver*, *tin*, *lead*, *bismuth*, *cadmium*, and *zinc*, but not so readily with *iron* or *copper*, yielding thereby an interesting class of bodies known as *amalgams*; and its application for the amalgamation of gold and silver in the extraction of these metals, will be treated of in the chapters on these metals. Mercury does not decompose water, but Wiggers and others state that the metal is dissolved to a small extent upon continuous boiling with water; and with *chlorine*, *bromine*, *iodine*, or *sulphur*, the metal may be directly combined at ordinary temperatures. *Hydrochloric acid* is without action upon mercury, even when the concentrated acid is heated with the metal; but *nitric acid* dissolves it, with the evolution of nitric oxide, and the formation of mercuric or mercurous nitrate, according to the proportion and concentration of the acid employed; while the metal is scarcely affected by dilute *sulphuric acid* in the cold, but if the concentrated acid be heated with mercury, then sulphurous anhydride is copiously evolved, and mercuric sulphate is formed. Thus—



As already stated, mercury and chlorine unite at the ordinary

temperature, but their union is much more rapid at the volatilising point of the metal. All the compounds of mercury are either decomposed or volatilised by heat, and all yield metallic mercury on fusion with sodic carbonate.

The commercial metal, unless specially purified, is frequently contaminated with small quantities of the volatile metals, zinc and bismuth, which are sometimes associated with the ores of mercury, and distil over with the latter in its extraction; while lead, antimony, tin, and bismuth, are also added as adulterations of the metal, but the comparative purity of the metal is readily observed by allowing a drop of it to run down an inclined surface, when it ought to roll as a perfect sphere, and not elongate or drag a tail behind it; or on shaking in a bottle or flask, along with air or oxygen, it should retain its metallic lustre unimpaired, and without the deposition of any grey or black powder, while further, when dissolved in nitric acid, and the solution evaporated to dryness and ignited, the metal, if pure, leaves no residue of oxide. The atomic weight of mercury is 200, and its chemical symbol Hg (Hydrargyrum).

The chief applications of mercury are in the amalgamation processes for the separation of gold and silver from their ores, or the gangue with which they are mixed; in the construction of barometers, thermometers, and other philosophical instruments; and for the purposes of gilding, plating, etc.; while the metal and its compounds are of considerable application in pharmacy and anatomy.

87. Water Gilding.—Before the introduction of the process of electro-plating or electro-gilding, it was the practice to gild ornamental articles of copper, bronze, etc., by a process known as *water* or *wash-gilding*; a process depending upon the facility with which gold may be amalgamated or dissolved in mercury, and the ready manner in which the latter metal is subsequently expelled upon the application of heat, so that bodies whose surfaces have been suitably prepared and coated with the gold amalgam, and afterwards gently heated, are thus left coated with a thin adherent film of gold, the mercury having been driven off by the heat. For the purposes of water-gilding, the gold amalgam is first prepared by very gently heating some 6 or 8 parts of mercury

with one of gold, whereby a fluid amalgam is obtained which yields, on pressure and filtration through wash-leather, a pasty mass or amalgam containing about 2 parts of mercury to 1 of gold, the excess of mercury having been expelled by the pressure, and this resulting amalgam is the one employed in gilding; but, before its application, the surface of the object to be gilded requires to be thoroughly cleaned, and for this purpose it is first heated to redness in a charcoal fire, then plunged into dilute sulphuric acid, rubbed with a hard brush, and washed with water, occasionally also being afterwards immersed for a few minutes in strong nitric acid, when it is again washed and dried. The surface thus cleansed is then amalgamated or coated with a film of mercury, by rubbing or washing it with a solution of mercurous nitrate, after which the gold amalgam is applied by pressing or rubbing the article upon the pasty amalgam, which thus attaches itself to the prepared surface. The article is then washed, and the mercury expelled by heating over a charcoal fire, the surface being kept uniformly coated during this operation by a continued rotation and brushing with a soft brush, the heating being continued until the surface assumes a dull yellow colour, when the article is removed and polished upon a revolving brush slightly damped with vinegar, or upon a wet burnisher of haematite. A mixture of bees'-wax, red-ochre, cupric acetate (verdigris), and alum is then applied for the removal of the last traces of mercury remaining on the surface, and at the same time to impart a redder shade to the surface; after which the article is burnished, washed with dilute nitric acid, then with water, and finally dried.

88. Silvering of Mirrors.—The silvering of mirrors, reflectors, etc., is effected by coating one surface of the glass plate with an amalgam of tin and mercury containing about 20 per cent. of the latter. The silvering is effected by first carefully covering the surface of a perfectly smooth slab or stone, somewhat larger than the size of the plate to be silvered, with a sheet of tin-foil, taking care to remove all creases therefrom, and to expel all air bubbles from beneath the tin by carefully smoothing it over with a brush, while around the slab or table is placed a gutter or channel for collecting the excess of mercury as it runs off; and the table

itself is swivelled upon an axis, so that it can be inclined at any angle with the vertical by actuating a screw. The table is now placed perfectly horizontal, and the tin-foil is amalgamated with mercury by pouring a small quantity of the latter upon the surface of the tin, over which it is spread by means of a piece of flannel; upon this surface is then poured a very thin layer of mercury, after which the plate of glass, perfectly clean and dry, is very carefully pushed forward from one edge across the table, so as to prevent any air getting between the amalgam and the glass, and at the same time the plate carries before it the superfluous mercury; after slightly inclining the table to drain off the excess of mercury, a series of heavy weights are placed upon a blanket covering the plate, and it is allowed to stand thus weighted for about 24 hours, after which the inclination of the table is gradually increased from day to day so as to drain away the mercury. After the weights have been removed, the silvered plate is placed upon a sloping table, the upper edge of which is gradually raised until the table attains to the vertical position.

89. Mercury and Oxygen.—These elements yield by combination two oxides known as the mercurous and mercuric oxides respectively.

Mercurous oxide (Hg_2O), known also as the black oxide, is an unstable body obtained as a brown-black, inodorous, and tasteless powder on the addition of an excess of caustic potash to a solution of a mercurous salt; or by treating finely-powdered calomel (Hg_2Cl_2) suspended in water with an excess of the same re-agent; in either case the precipitate requires well and careful washing to free it from potash, which washing must be accomplished in the dark, since this oxide is resolved into mercuric oxide (HgO), and metallic mercury on exposure to sunlight. Mercurous oxide is insoluble in water, and is resolved into its elements on heating to redness; it forms a detonating mixture with phosphorus, and it is decomposed on treatment with phosphorous acid, phosphuretted hydrogen, or when boiled with an aqueous solution of potassic iodide, in each case yielding metallic mercury. It is soluble in acids, producing thereby a series of mercurous salts.

Mercuric oxide, or *red oxide of mercury* (HgO), is the most important oxide of mercury; it is produced when mercury is heated to its boiling point, and exposed for a considerable time to the influence of atmospheric air or oxygen, care being taken that the temperature be not raised sufficiently high to again decompose the oxide; it is also prepared by heating mercurous or mercuric nitrate at a gradually increasing temperature, until nitrous fumes cease to be evolved; or in the wet way by adding an excess of potash to a mercuric salt, and afterwards carefully washing the precipitate. Mercuric oxide varies somewhat in physical characters according to its mode of preparation, but, as generally occurring, it is a crystalline, granular, or scaly powder of a bright or brick-red colour, changing to yellow on pulverization, the tint decreasing in intensity with the fineness of the powder; while the precipitated oxide is of an orange yellow colour. This oxide has a disagreeable metallic taste, is highly poisonous, and is but very slightly soluble in water. On gently heating, its colour changes to vermillion red and then to black, recovering its original colour on cooling; but by exposure to a red heat it is resolved into oxygen and the vapour of mercury, which latter condenses in the cool part of the apparatus, and is partially reoxidized by the heated oxygen. Chlorine decomposes this oxide at a red heat, with the evolution of oxygen and the production of mercuric chloride, but at a lower temperature hypochlorous acid and mercuric chloride are produced. It is reduced to mercurous oxide by ferrous salts or ferric hydrate, and is soluble in acids, producing thereby a class of mercuric salts. The commercial oxide is frequently contaminated and adulterated with basic *mercuric nitrate*, *cinnabar*, *brick-dust*, *minium* or *red-lead*, or with *nitre*.

90. Mercury and Sulphur.—Mercury forms two compounds with sulphur, known as mercurous and mercuric sulphides respectively; the former, obtained as a black precipitate when sulphuretted hydrogen or ammonic sulphide is passed into a solution of a mercurous salt, is not of metallurgical importance.

Mercuric sulphide (HgS) is metallurgically the most important compound of mercury. As native *cinnabar* it constitutes the chief ore of the metal, and the pigment known

as *vermillion* is a crystalline form of the same body obtained commercially by the sublimation of the amorphous substance. When mercury and sulphur are rubbed together for a considerable time, there results a black powder, constituting the amorphous variety of mercuric sulphide; and this, if heated in a closed vessel, yields a crystalline sublimate of a red colour (cinnabar), which, if again pulverised, produces a dirty red powder; while the black amorphous sulphide is also precipitated on the addition of an excess of sulphuretted hydrogen to a solution of a mercuric salt, which precipitate on drying, and subliming as before, again yields cinnabar.

The *vermillion* of commerce varies much in tint and purity of colour, slight differences in the details of its manufacture impairing or improving its colour, and hence the products of certain localities are especially prized: thus the vermillion imported from China, Holland, etc., is of superior quality. The method of preparation of the last-mentioned variety, as pursued at Amsterdam, consists in gradually adding about 370 lbs. of mercury to 50 lbs. of sulphur kept melted in an iron pot, the mixture being effected by careful stirring with an iron spatula, after which the fused charge, consisting of mercurous and mercuric sulphides with an excess of sulphur, is poured on to an iron plate, then broken up on cooling, and distributed among a number of small jars, each capable of holding about $1\frac{1}{2}$ lb. The product is then sublimed in earthen vessels, about four feet in height, closed at their lower ends, and glazed on the inside, of which three are placed in a furnace constructed so that the flame plays around and heats the cylinders to about two-thirds of their height; when the lower ends of the cylinders have thus attained to redness, the contents of one of the small jars previously mentioned is thrown into each vessel, an operation attended with the inflammation and volatilization of the excess of sulphur, the flame, on the introduction of each fresh portion, rising for a short time to a considerable height above the mouths of the jars, and upon the subsidence of which, a smooth cast-iron plate is placed upon the mouth of each vessel for a short time, before the addition of the contents of another small jar, the emptying of the jars in this manner continuing for from 30 to 36 hours. When the cylinders have received their full charge they are

covered over, and the heat maintained during a further period of 36 hours, occasional stirring of the mass being effected with a bar introduced through an aperture in the covering; and the sublimate of cinnabar collected on the cover plates, after the addition of each jar to the cylinder, is detached as it collects; while at the conclusion of the process, the cylinders are withdrawn from the furnace, broken up, and the cinnabar collected around their upper portions is detached, and, along with that from the covers, then requires to be ground, sifted, washed and dried, to fit it for the market. The Chinese method* of preparation consists in subliming in an earthen vessel a mixture of one part of sulphur with four parts of mercury, the vessel being covered with an iron plate, kept moist and luted on. The heat is continued for some 24 hours, upon which the vessel is broken up after cooling, and the purer separated from the inferior portions of the sublimate, the purer portions being pounded and sifted into a large vessel containing water, when a scum rises to the surface, which is poured off along with the water. The washing is twice repeated, when the sediment or residue in the bottom requires drying, and is then ready for sale.

Various wet methods are also described for the preparation of vermillion: thus the black sulphide obtained by the precipitation of a salt of mercury with sulphuretted hydrogen, is converted into the red variety by heating it with an alkaline persulphide; the same product likewise results on treating the black powder produced by the trituration of sulphur with mercury, with a solution of potash, and heating at a carefully regulated temperature of from 45° C. to 50° C. during several hours, then washing, and separating any metallic mercury by levigation.

Mercuric sulphide, or *cinnabar*, may be obtained crystallised in forms of the hexagonal system. It is transparent, of a cochineal red colour with a scarlet powder, which, by heating in a retort, or out of contact with the atmosphere, becomes brown and then black, again recovering its scarlet colour on cooling if the heat has not been too long continued; but in contact with the air the sulphide burns with a bluish flame, yielding sulphurous anhydride and metallic mercury. Nitric

* *N. Edinburgh Journal of Science.*

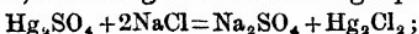
acid has only a feeble action upon it in the cold, while aqua-regia attacks it vigorously with the production of mercuric chloride ($HgCl_2$). If heated with charcoal, iron, tin, antimony, or several other metals, it yields metallic mercury; caustic alkalies, alkaline carbonates, and lime also liberate mercury at a red heat, with the formation, in the case of the latter, of a calcic sulphide and sulphate, thus—



It is also reduced by heating in hydrogen, with the liberation of sulphurctted hydrogen. The commercial varieties of this compound are frequently adulterated with brick-dust, ferric oxide, red-lead, etc.

91. Mercury and Chlorine.—These elements combine slowly at the ordinary temperature, but more rapidly under the influence of heat, combining in two proportions, yielding thereby a mercurous and mercuric chloride respectively.

Mercurous chloride (Hg_2Cl_2), known also as *calomel*, is a white, tasteless, inodorous, and heavy powder, becoming dark grey on exposure to light, and acquiring a yellow tint on the application of heat; it volatilises below redness without previous fusion, and is practically insoluble in water. It is of extensive application in medicine. Mercurous chloride may be prepared by a variety of both dry and wet methods; it results on the trituration of four parts of corrosive sublimate ($HgCl_2$) with three parts of mercury, the rubbing being continued until the mercury entirely disappears; while the process is facilitated by moistening the mixture with water or alcohol, but the product so obtained requires sublimation, with subsequent pulverization and washing with hot water, to entirely free it from the mercuric chloride which may have sublimed along with it. The dry method, more usually adopted for its preparation, consists in subliming a mixture of equal parts of mercurous sulphate and common salt, when double decomposition occurs, with the production of sodic sulphate and mercurous chloride, according to the following equation—

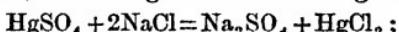


but according to whichever method prepared, it still requires careful washing with warm water, or a little alcohol, to free it from other and soluble mercurial compounds with which the

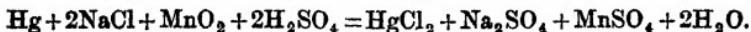
sublimate is contaminated. Mercurous chloride may be produced in the *wet way* by precipitating a mercurous salt with a soluble chloride, or by dissolving mercurous oxide in hydrochloric acid.

Mercuric chloride ($HgCl_2$), or *corrosive sublimate*, is a white or colourless, translucent, crystalline body, possessing a disagreeable metallic taste; it is more volatile than the mercurous chloride, and is soluble in water, alcohol, and ether. It is a very powerful poison; it is decomposed upon heating with *arsenic*, *antimony*, *bismuth*, *zinc*, *tin*, *lead*, *iron*, or *copper*, with the production of mercurous chloride (Hg_2Cl_2) and mercury, or an amalgam of mercury with the excess of the other metal, along with a chloride of the metal employed; thus if antimony be employed, the products are antimonious chloride and metallic mercury; and tin heated with mercuric chloride yields a sublimate of stannic chloride, and a residue of mercurous chloride with stannous chloride.

Mercuric chloride occurs native, but may be prepared artificially by heating mercury in an excess of chlorine gas, by dissolving mercuric oxide in hydrochloric acid, or, as is more general on the large scale, by the decomposition of mercuric sulphate, by heating it in admixture with an equal amount of common salt at a gradually increasing temperature, when the mercuric chloride sublimes and condenses in the cool part of the apparatus, according to the following formula—



while to prevent the formation and sublimation at the same time of a small proportion of mercurous chloride (Hg_2Cl_2) (calomel), a little peroxide of manganese is added to the mixture, or a mixture of mercury, sodic chloride, peroxide of manganese and water, may be triturated together and subsequently subjected to heat, when mercuric chloride sublimes, and the sulphates of soda and manganese remain behind; thus,



This compound also results when mercuric oxide is dissolved in hot hydrochloric acid, the crystals of mercuric chloride separating as the solution cools. This salt is extensively used for the preservation of anatomical specimens, and wood is sometimes soaked in an aqueous solution of this salt to

prevent its rotting in situations where its surface cannot be protected by paint, etc.

92. Amalgams.—Mercury unites with most of the metals if brought into contact with them, especially if the metals be in a fine state of division, the union sometimes, as with *potassium*, *sodium*, *bismuth*, *cadmium*, *tin*, *zinc*, etc., occurring at the ordinary temperature, while other metals require the assistance of heat, and the bodies resulting from the union of mercury with another metal constitute a somewhat extensive series of bodies designated “*amalgams*,” some of which are of extensive application in the arts. To such belong the amalgams of mercury and tin employed in the silvering of mirrors; mercury with gold and silver employed in gilding, and the amalgam with tin, gold, and silver used in dentistry. The amalgams exist sometimes in the fluid state, at others they assume the solid form, but generally the liquid amalgam is but a solution of the solid and more definite combination of mercury and another metal, in an excess of mercury, which excess can be frequently separated by simple pressure through chamois leather, the solid amalgam left thereby in many cases appearing to have a definite atomic composition; and this has led to the consideration of the true solid amalgam as having an atomic chemical constitution, in which however, the chemical affinities between its constituent metals are only very feeble. The amalgamation of silver or copper is attended with considerable diminution in bulk, but generally the union is accompanied by little or no diminution in volume. The consideration and description of the amalgams produced by mercury, with the metals antimony, bismuth, and platinum, are treated of in Vol. I.

The amalgamation of *mercury* with *iron* cannot be readily and directly effected; but by introducing sodium amalgam, containing one per cent. of sodium, into a clear saturated solution of ferrous sulphate, a viscid amalgam is obtained, which, in small globules, is attracted by the magnet.

Sodium combines with mercury readily at the ordinary temperature, the union being attended with the production of heat, light, and a hissing sound. The amalgam may be prepared by the trituration of the two metals in a dry mortar fitted with a cover. When the amalgam contains about 30

parts of mercury to 1 of sodium, it forms a compound which is liquid at a moderate heat, but at the ordinary temperature yields a granular, tolerably hard solid, which may be filed into a powder, while with one per cent. of sodium it is viscid, and consists of a solid and liquid portion. This amalgam is employed as a medium for effecting the amalgamation of iron, platinum, etc.; it is also exported for the amalgamation of gold and silver, in which application it is said to facilitate the amalgamation, and to prevent *flouring* of the mercury.

An amalgam of *copper* results when copper-foil is introduced into a solution of mercuric nitrate; upon triturating mercury with common salt and cupric sulphate; by treating a solution of cupric sulphate with sodium amalgam, and in a variety of other ways. This amalgam possesses the peculiar property, that, when left to itself for a few hours, it hardens, so that it may be pulverised, while its pasty and elastic character can be again restored by continued kneading or pounding of the amalgam, although its density remains the same both in the hard and soft states.

Zinc is slowly amalgamated with mercury by triturating zinc filings with mercury at the ordinary temperature, but the combination is effected most readily if the temperature be raised, the amalgamation of these metals being usually effected by pouring a fine stream of mercury into zinc melted at the lowest possible temperature, while keeping the melted metal constantly stirred. The amalgam of these metals, containing about 20 per cent. of mercury, is sometimes employed for coating the rubbers of electrical machines. It is a tin-white, granular alloy, brittle, and pulverulent, burning at a red heat. It decomposes neutral salts of manganese, iron, chromium, cobalt, nickel, and copper, and liberates hydrogen when immersed in caustic potash.

Tin and mercury unite readily even at ordinary temperatures, but much more vigorously at the melting point of tin, the resulting amalgam having a tin-white colour, and is more or less brittle and granular, according to the proportion of mercury present. An amalgam of these metals is employed in the silvering of mirrors.

93. Ores of Mercury.—Mercury is often found in the native state, also as iodide and chloride, and in union with gold

and silver as amalgams; but its combination with *sulphur*, constituting *cinnabar*, forms the most important ore of the metal, and that from which almost the whole of the mercury of commerce is obtained; yet, mercury has also of late been collected from certain fahl-ores containing silver, copper, etc., accompanied by more or less mercury.

The ores of mercury occur in both ancient and modern geological formations; thus while the deposits at New Almaden in California occur in rocks of cretaceous age, and at Idria in limestones of jurassic age, yet many deposits of this metal occur in rocks of silurian age.

Mercury often occurs *native* as globules disseminated throughout its ores or gangue, the mines of Almaden, Idria, Hungary, and Sweden, thus yielding the native or virgin metal. The native metal is almost pure, sometimes, however, containing traces of gold and silver.

The *native mercuric sulphide*, or *cinnabar*, is a cochineal or brownish-red transparent mineral, possessing an adamantine lustre, a scarlet streak, and a hardness of from 2 to 2·5. It crystallises in hexagonal forms, but by sublimation it is obtained in fibrous masses; it is sectile, has a subconchoidal fracture, a specific gravity of from 8·0 to 8·1, and changes upon heating from red to brown, and then to black, recovering its scarlet colour on cooling, provided the temperature employed has not been too high. This mineral often occurs nearly pure, yielding from 75 to 85 per cent. of mercury; while varieties found at Almaden, Idria, etc., contain from 40 to 50 per cent. of gangue or foreign matters, with from 40 to 50 per cent. of mercury. The more important mines in which cinnabar occurs are those of Idria in Illyria, and Almaden in Spain: at the former it occurs disseminated through a bituminous schist, limestone, or grit; while at Almaden it is found in veins traversing a micaceous schist. Other localities in which it occurs are Bavaria, Bohemia, Hungary, the Ural and Altai mountains, China, Japan, Mexico, Southern Peru, Coquimbo, Chili, and California.

The native compound of *silver* and *mercury*, known as "*amalgam*," is a silver-white, opaque, brittle body, which occurs either massive, or crystallised in forms of the regular system. It has a silver-white streak, a conchoidal fracture, a

hardness of from 3 to 3·5, and a specific gravity ranging between 10·5 and 14. Specimens from different localities vary widely in composition, containing from 13 to 36 per cent. of silver, with from 87 to 64 per cent. of mercury, and at other times it is also associated with gold. Amalgam is found in the Palatinate, Hungary, Sweden, Spain, Dauphiné, Chili, Peru, etc.

Mercurous chloride, or *horn-quicksilver*, is found associated with cinnabar at Idria, Almaden, the Palatinate, etc., where it occurs crystallised or granular, of a dirty white or ash-grey colour, with a yellowish streak. It has a hardness of from 1 to 2, and a specific gravity of 6·482. *Iodides* and *bromides* of *mercury* are also found, but more rarely.

Selenides or *selenio-sulphides* of mercury, of a steel or lead-grey colour and metallic lustre, also occur occasionally, accompanying other ores of mercury, in Mexico, the Hartz, etc.

EXTRACTION OF MERCURY FROM ITS ORES.

The methods employed in the extraction of mercury are all processes of distillation, in which the ore, mixed with lime, iron, iron and lime together, or ferric oxide (smithy scales), is heated in a closed distillatory apparatus; or as still pursued at Almaden and Idria, where the ore occurs disseminated in a schistose rock, rendering it necessary that large quantities of the materials be operated upon, it is heated alone in an apparatus admitting an amount of air sufficient to convert the whole of the sulphur contained in the ore into sulphurous anhydride; while in the former case, where lime is used, the sulphur is removed in combination with lime, as calcic sulphide and sulphate, according to the equation of page 197; and if ferric oxide be employed, then ferrous sulphide and sulphurous anhydride result. The method pursued in extracting the metal thus depends upon the *nature* and *amount* of the foreign matters contained in the ore, and also whether the ore be in the state of powder, or is more or less massive, and also upon the cost of fuel, etc. Yet all the methods pursued may be classed under one of two classes, viz., 1°, *air reduction processes*, in which the decomposition is effected by roasting the ore, either in *mounds*, *kilns*, or *reverberatory furnaces*; 2°, reduction of the ore (*cinnabar*) by means of *lime*, *iron*, *iron scales*, etc.

AIR REDUCTION PROCESSES.

94. Huancavelica or South American Process.—The ore here treated by the air reduction process is cinnabar, more or less diffused through sandstone. The furnace or kiln employed consists of a small shaft resembling a small blast or cupola furnace, and which is built of any common refractory material that occurs in the neighbourhood; the fireplace, in which the herbage is consumed as fuel, is situated in the bottom of the furnace, and its arched roof contains numerous openings through which the smoke and heated gases ascend, while immediately above the arch is an opening or doorway, closed during the working of the furnace, but opened at the conclusion of the distillation for the withdrawal of the spent residues. Just below the top or mouth of the furnace a number of channels (usually three in number) open into the furnace, and each of these is connected with a series or system of earthen pear-shaped vessels or condensers known as "*aludels*," in the hollows of which the mercury, volatilised from the charge of materials in the furnace, condenses and is collected, since the top of the furnace or stack is closed after the furnace has been lighted and begun fairly to burn.

The furnace is charged by piling the larger pieces of ore upon the perforated arch over the fire, upon which pieces are laid the smaller fragments, and so on to the top, the smalls (powdered ore) being moistened with water and roughly moulded by women into bricks, which are then piled in the furnace; but it is necessary, in charging the furnace, that the materials be arranged so as to secure a draught through it. When the furnace is thus charged, and while the top is still uncovered, a fire is made in the fireplace, when, as soon as the lower portion of the furnace has become heated and a draught through the furnace thoroughly established, the top is closed by stones and earth, when the smoke and other volatile products are thus compelled to pass through the system of aludels already mentioned, where the mercury is condensed and collected. The reduction is thus effected by the agency of heat and air, the latter oxidizing the sulphur, converting it thereby wholly into sulphurous anhydride, with traces of sulphuric acid. The charge of ore is

32 quintals, and the time of working each charge, including the time of charging, is about twenty-four hours; but the average yield is only from 12 to 15 lbs. of metal per quintal of ore, a loss to the extent of almost one-half of the metal contained in the ore arising from defective construction of furnaces, the want of repairs, whereby cracks and fissures are allowed to exist in the structure, together with an imperfect roasting or exhaustion of the ore, the upper portions of the charge frequently being scarcely acted upon; but the method requires less time and fuel than when fluxes are employed and the distillation effected in closed retorts.

95. Almaden Process. — This process, pursued at the Almaden mines of Spain, differs from the last described only in the construction of the furnace, which consists of a square, round, or polygonal furnace, or heating chamber *a*, fig. 40, about four feet in diameter, and divided near the middle of its height by a perforated brick arch into two chambers *a*, *b*, the lower one of which forms the fireplace, while the charge is introduced into the upper one, or ore-chamber as it is called.

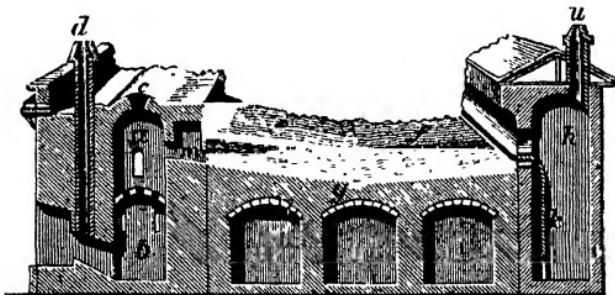


Fig. 40.—ALUDEL FURNACE EMPLOYED AT ALMADEN.

The charge is introduced partly through the door at the back of the furnace, and partly through the opening *c* in the roof, while the lower chamber further communicates with a stack *d*, situated near to and at one side of it, and with which the fire is put into communication on first starting the furnace, so as to get up the draught; but when active combustion has commenced, this communication is closed by a damper, and the gaseous products of combustion pass upwards through the chamber above containing the ore, and from thence through

openings *m* into the system of earthenware condensers called "aludels," each measuring about 18 inches in length; these being arranged in rows of chain-like order upon the two slopes of brickwork *e, f*, of the arched terrace or *aludel bath*, along the lowest point of which, and running its full length, is the bottom channel or gutter *g*, for the collection of the metal escaping from an aperture made in the under side of the lowest aludels of



Fig. 41.—ALUDELS SHOWN TO A LARGER SCALE.

the series. The uncondensed products which pass through the aludels are conveyed into the large chamber *h*, in the bottom of which is placed a tank of water, the gases and vapours on their entry being deflected by the screen *k* to the bottom of this chamber, whereby the removal of any condensable portions is effected before the gases make their escape to the atmosphere through the short chimney *u* in the roof of the chamber. The total width of this arrangement of furnace and condensers is about 65 feet; and the fuel consumed in the fireplace *b* is brushwood, etc. The arrangement of aludels comprises from 500 to 600 of these latter vessels, arranged in twelve rows on each slope of the aludel bath or terrace, as is shown in fig. 40, the small end of each aludel being inserted and luted into the larger extremity of its successor, the operation of luting their joints with clay, and emptying of each vessel separately at the conclusion of the distillation or firing lasting about twelve days, is necessarily a work occupying considerable time, and thus renders the process exceedingly extravagant in the item of labour.

The charge to the extent of some 10 or 14 tons is assorted so as to yield about 10 per cent. of its weight of mercury, and is introduced into the ore-chamber *a*, by placing upon the perforated arch of the fireplace, or floor of the chamber, the poorer portions of sandstone broken into the largest pieces, upon which are then placed smaller fragments of richer ore, above which again is placed the smaller pieces of poor ore, and finally, at the top is introduced the dross, soot, etc., collected from the aludels and condensing chambers, along with the smalls (fine powdered ore), the latter being moulded with clay and

lime into bricks. Care is taken in charging, as in the previously described process, that the materials are so disposed as to permit of a current or draught passing upwards from the fire through the ore, and so into the condensing arrangement of aludels. When the furnace is thus charged, the aperture *c* in the roof, the charging doors, etc., are closed and luted, upon which the fire is lighted by opening a communication with the stack *d*, which, as soon as combustion has fairly started, is closed by a damper, and the firing then continued during about twelve days, during which time the flame and air pass through the ore-chamber, whereby the sulphur of the ore is converted into sulphurous anhydride, accompanied by a little sulphuric acid, while the mercury volatilises and is largely condensed in the hollows of the several aludels, of which those forming the lowest portion of the series, situated over the channel or gutter *g*, are provided with an aperture to allow of the escape of the collected metal into the channel which communicates by a pipe with a receiver beneath. When the process or firing is completed, the whole is allowed to cool, and the aludels are then removed singly and their contents emptied into the central channel *g*, and so conveyed to the receiver.

This process, as already noted, is wasteful in labour and fuel; also, if the ore mixture be too rich, there is a considerable loss of mercury, attended with injury to the health of the workmen.

The metal collected from the receivers and condensing chambers is much contaminated with mechanical impurities, as soot, dross, dirt, etc.; and for the separation of these, the metal is poured upon the upper end of the floor of a room which inclines slightly from one end to the other, so that the metal, in running slowly down to the receivers, deposits upon it a large proportion of these mechanical impurities.

96. Idrian Process.—The ore occurs at Idria in limestone, or in a bituminous schist or slate, and the furnace employed forms a building about 180 feet long and some 30 feet high, consisting of a central portion or furnace proper, with the air passages for supplying air for the combustion and oxidation of the charge; while upon either side of this furnace is erected the condensing arrangement of six chambers, *a*, *a*, *a*, etc., communicating with each other by openings situated

alternately near the top and bottom of the chambers, whereby the current of gases and condensable vapours are made to circulate up and down through each chamber to the end of the series, the last one being often provided with a number of inclined projecting boards or ledges placed upon the walls, so as to reach from one side almost to the opposite one, the connections being made alternately with one wall and then the other, thus dividing the tower into a very tortuous flue. The gases and vapours, in passing from the furnace, are introduced into the condensing chambers, where their velocity is considerably reduced, owing to the large size of the condensers with relation to the flues from the furnace, which reduction of velocity favours condensation, and also permits the adhesive action of the walls to come more into action for the separation of any solid particles which may be carried along with the gaseous current; while the projecting ledges in the last tower are kept continually moist by a current of water flowing over them, and here are arrested the last portions of solid or condensable matters before the gases escape to the atmosphere.

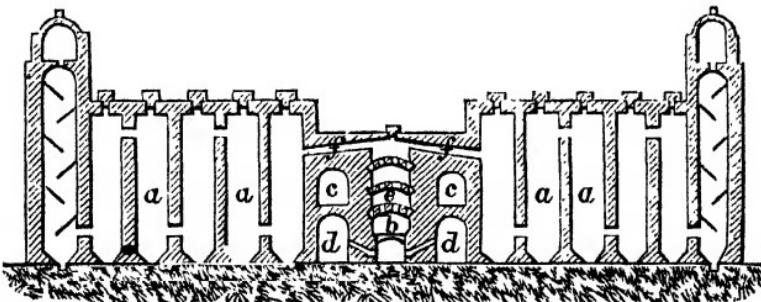


Fig. 42.—IDRIAN FURNACE AND CONDENSING CHAMBERS.

Each of the chambers, *a*, *a*, is provided with an opening at the top, which is kept closed during the working of the furnace, as is also an outlet from the bottom by which the condensed metal is conveyed to the main tank. The bottom of the condensing towers is formed of iron plates or of stones, which slope from the sides towards a median line, and also from back to front towards the opening, for the withdrawal of the condensed mercury. The furnace itself consists of a chamber divided vertically by three perforated brick arches into four

compartments, the arches serving to support the different varieties of ore in the furnace: thus the lowest chamber *b* constitutes the hearth where the fuel is consumed, *c, c, d, d,* being arched passages or flues conveying warm air to the furnace and to the materials in the upper chamber for the oxidation of the sulphur and bituminous matters in the ore; while the upper chamber communicates by two lateral passages, *f, f*, with the series of condensers. In *e* are placed the largest pieces of ore, of varying degrees of richness, from the poorest, yielding only about 1 per cent. of mercury, to the pure sulphide yielding 80 per cent.; the poorest, however, being first introduced so as to be nearest the fire. Upon the second arch are deposited the smaller pieces and fragments of ore from the mine, these being still sufficiently large to permit of the free ascent of the gaseous current through the furnace; while upon the uppermost arch are placed a number of earthen trays or pots filled with the fine powder or schlich obtained from the washings, along with the dust and condensed cinnabar collected in the condensers, and returned to the furnace for redistillation. In this manner the furnace contains, when charged, altogether about 55 tons of materials, yielding from 8 to 10 per cent. of mercury.

The materials for the charge are introduced through side doors into each of the chambers, which doors are luted up when the charging is completed, and remain so during the conduct of the process, which usually continues from 24 to 30 hours.

The furnace requires five or six days to cool down, after the distillation is completed, before the apertures are opened for withdrawing the condensed mercury, and the chambers entered to brush down the *mercury, cinnabar, and mercurial soot* collected upon the walls of the condensers; the last named operation being attended with considerable injury to the health of the workmen, owing to the inhalation of mercurial vapours producing salivation and nervous tremblings.

The process is conducted by charging the furnace and closing all apertures in the manner described, when a brisk fire of timber (usually beech) is made upon the hearth, whereby the furnace will attain to a cherry redness in some 12 or 15 hours, when the air from the side chambers or flues, *c, c, d, d,* and gases from the furnace are drawn by the draught over the

heated ore, whereby the sulphur of the ore is oxidized with the separation of the mercury, which, at the temperature produced by the heat of the furnace and the combustion of the sulphur in the ore, is vapourised, and passing along with the gaseous current by the flue *f*, *f*, enters the condensing chambers, and is there collected in the manner detailed above. The temperature for a certain period at the commencement of the process continues to rise, owing to the combustion of the sulphur in the ore, and the condensation accordingly extends further along the series of condensers, large quantities of mercury being collected towards the end of the series, while at the commencement and conclusion the major portion of the metal condenses in the first tower from the furnace. The whole period of volatilization extends over about twelve hours.

The mercury collected in the receivers from the condensing chambers is then filtered through cloth for the separation of its mechanical impurities, after which it is placed in cast-iron bottles, holding from 60 to 70 lbs. each, and is then ready for exportation.

97. Hähner's Modification of the Idrian Furnace.—The Idrian process as last described *is not continuous*, but requires to be stopped for about five days after working off each charge, to allow the furnace to cool down before admitting of the removal of the spent ore, etc.; and to obviate this, the modification of Hähner has been introduced within the past few years at New Almaden in California. Hähner's furnace consists of a circular reduction chamber *a*, about 3 feet 8 inches in diameter, and 18 feet in height, communicating near its upper end with a series of six condensing chambers, *b*, *b*, the refrigeration of which is further promoted by making the roof to form the bottom of an iron tank, cooled by water circulating through it; or of iron plates kept cool by a stream of water, while the walls of the chambers are coated with a stucco of mortar and fine sand, so as to present a hard and non-absorbing surface, since in the Idrian arrangement it is found that much mercury is absorbed by the walls, and lost through cracks and fissures. The communication between the reduction chamber and the first condensing chamber is controlled by a stop or sluice valve *c*, while the circulation in

the condensers is as described in the Idrian furnace, communication between the chambers being made alternately at the top and bottom of the division walls; while the current is maintained by the draught from a chimney, built in three tiers, in each of which are formed ledges or terraces, kept cool by a flow of water over them, and so arresting the last portions of the condensible matters.

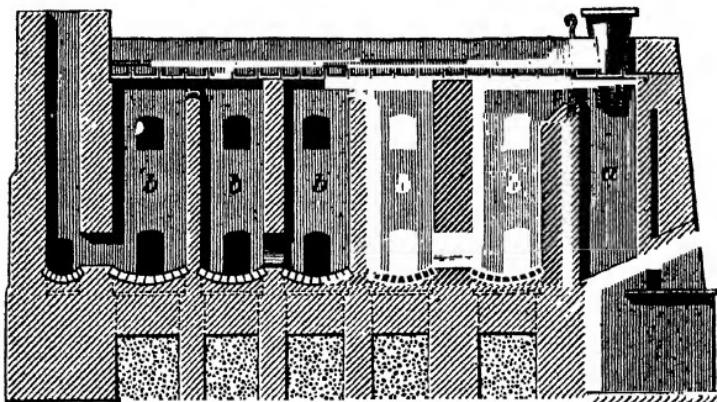


Fig. 43.—HAHNER'S MODIFICATION OF THE IDRIAN FURNACE.

The ore, broken into pieces of the size of the fist, is introduced into a hopper in the top of the reduction chamber, from whence, by the withdrawal of a slide in the bottom, it is allowed to fall into the chamber; so that the charge of about 7 cwt. of ore, along with from 3 to 5 per cent. of charcoal, requiring to be charged every 45 or 50 minutes, can be introduced into the reduction chamber without any communication being made between the atmosphere and the furnace; while the spent ore is withdrawn from the bottom of the chamber or furnace by an arrangement of movable bars, whereby the spent materials fall out by their own gravitation, or are assisted by a rake.

Before the furnace is ready for its regular and proper charges of ore and charcoal, as given above, it is necessary that the temperature of the furnace chamber be first gradually raised, and for this purpose a layer of bricks and wood is first placed upon the fire-bars so as to check the draught,

and prevent the ore from falling through; a layer of brushwood is next introduced, upon which is placed a layer of poor ore, then a layer of coal, which is covered by a layer of rich ore, succeeded by alternate layers of ore and fuel; this method of charging proceeds for about a couple of days, when the chamber will have become thoroughly heated, and the hopper charges of ore and charcoal begin to be introduced, and the ordinary continuous working of the furnace proceeds. The smalls obtained in working this process are treated in the Alberti furnace, described in the ensuing paragraph, since finely-divided ore can only be treated in the Hähner furnace, after mixing it with clay and moulding it into bricks.

98. Alberti Process.—This process is especially adapted to the treatment of *smalls* and *poor ores*, having been introduced at Idria for the working of ores containing but about 1 per cent. of mercury. The apparatus employed* consists of a reverberatory furnace consuming wood as its fuel, and which is connected with a series of large iron tubes and condensing chambers for the collection of the mercury and mercurial compounds volatilised during the roasting of the ore. The furnace *a*, figs. 44 and 46, has a sloping bed or hearth, divided during the working into three steps, on to which the ore is progressively raked from the flue towards the bridge end, and is thus subjected to a gradually increasing temperature; at the front end of the hearth is an aperture communicating with a chamber beneath, into which the ore is raked after having been transferred along the full length of the bed; while in the roof of the furnace, at the farthest end, is situated a hopper (*b*) fitted with a slide, by withdrawing which the charge falls on to the coolest portion of the hearth, where the ore undergoes calcination during a few hours, when it is raked forward to the middle portion of the hearth, and a further charge of ore is introduced from the hopper on to the cooler portion just vacated, and so on, the ore being thus calcined or roasted in three stages at a progressively increasing temperature. The gases and mercurial vapours from the hearth pass into the small brick condensing chamber *c* at the base of the stack, into which open two long, wide, cast-iron tubes *d*, passing backwards and inclining slightly down-

* *Annales des Mines*, Vol. V., 5th Series.

Fig. 45.

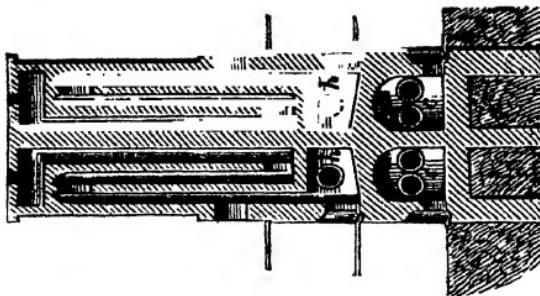
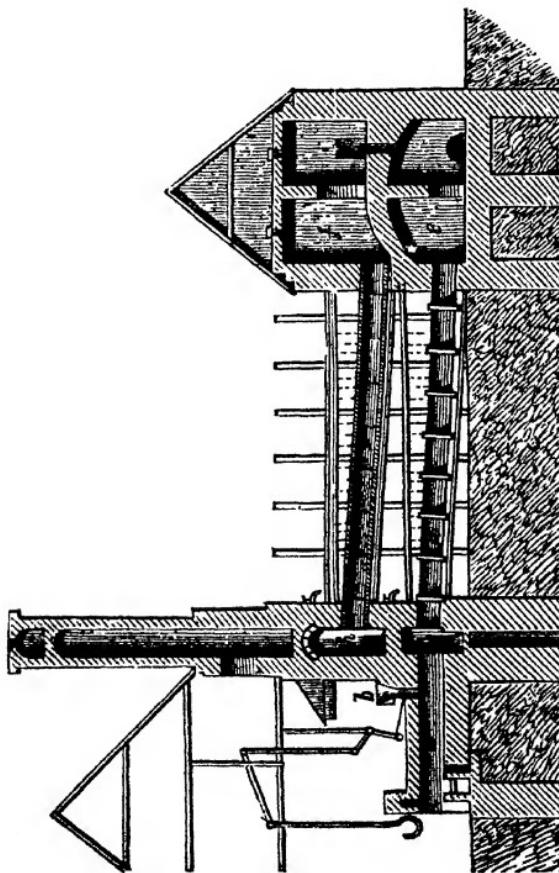


Fig. 44.



wards to a second condensing chamber of brickwork *e*, divided into an upper and lower storey; the vapours after circulating in the lower chamber *e* pass into the upper storey *f*, and from thence forwards along another iron tube *g*, opening into an upper chamber *h*, at the base of the flue, stack, or tower built above the furnace, and which is divided by a series of partitions, fig. 45, communicating alternately at the top and bottom, into a very tortuous course or flue, along which the products must circulate before reaching the atmosphere. The furnace is covered with a hood for the protection of the workmen; while the refrigeration of the condensing tubes *d*, *g*, of which there are two in the lower row and one in the upper, is promoted by running water upon their exterior from a series of jets communicating with a water tank situated above them.

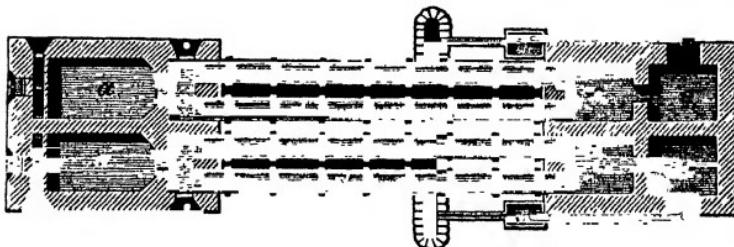


Fig. 46.—PLAN OF THE ALBERTI FURNACE.

About 3 tons of ore are treated at once in this furnace, which is introduced on to the hearth from the hopper in quantities of about a ton at a time, a charge of 1 ton being introduced each time that the portion nearest the fire-bridge is raked down into the chamber beneath, and the other portions each raked forward a stage. The doors and apertures are all closed and luted during the calcination or roasting, except at intervals, when they are opened to allow of the turning over of the charge.

The condensing arrangement of the Alberti furnace is much more perfect and scientific than those previously described, for by passing through the large chambers at *c*, *e*, etc., the velocity of the current is considerably diminished, favouring thereby the deposition of metallic or other matters carried in suspension; also the adhesion of the various surfaces upon

the condensed particles is made effective; and in this manner it is found that about 95 per cent. of the yield of mercury is collected in the lower of the iron tubes of the apparatus, and from which it is run into proper receptacles; while a large proportion of mercurial soot, containing metallic mercury along with vermillion or cinnabar, etc., is collected from the tubes, flues, and chambers, which is dried, and the metallic particles separated as perfectly as possible by raking it over an inclined plane so long as the metal continues to run out, after which the residue is returned to the furnace to be reworked with a subsequent charge.

The Alberti furnace is worked *uninterruptedly* for a period of six months, when the pipes are cleaned out, their lower ends having become almost stopped with an agglomerated dust or deposit containing from 40 to 50 per cent. of mercury, mixed with carbonaceous matters, etc., and the workmen who then enter the chambers to clean them out are clothed especially for the purpose, so as to be as impervious as possible to the deleterious action of the mercurial vapours.

99. Fahl-ore Process.—Fahl-ore, fahlerz, or grey copper ores frequently contain considerable proportions of mercury, which it is the object of this process to separate and extract. Accordingly in Hungary, where this process is pursued, the roasting of the copper ore is effected in mounds or heaps of some 40 feet in length, and so constructed as to admit of a moderate supply of air to the ore, for which purpose the site is first covered with a layer of small ore, upon which is superposed a layer of the larger pieces of such ore as has been already once roasted but not completely, upon this again is placed a quantity of wood and coal, then ore again; while the outside is formed by a coating of the powdered ore, which serves alike to check the passage of air through the pile, as also to arrest the particles of mercury as the latter is volatilised by the heat. The heap thus formed is then fired by igniting projecting pieces of the timber and coal of the pile, wherupon the sulphur of the ore breaks into combustion, with the production of sulphurous anhydride, when the heat produced by the fuel and burning sulphur volatilises the mercury, which is condensed and collected in the small ore forming the outer cover of the pile. The

operation thus proceeds for about three weeks, when the outer covering is taken down, sifted, and carefully washed, for the separation of the metal from the finer portions of ore with which it is associated.

METHODS OF REDUCTION WITH LIME, IRON, ETC.

These methods constitute by far the most scientific and skilful processes employed for the separation of mercury from its ores, permitting of the application of closed retorts for the distillation, with more perfect separation of the metal and exhaustion of the ore, while not necessitating the same exposure of the workmen to the poisonous influences of mercurial vapours; notwithstanding which, these processes are as yet only employed in the smaller works for the extraction of the metal, the great mines of Almaden and Idria still retaining the old, wasteful, and unhealthy processes already described.

100. Treatment of Mercurial Ores in the Gallery Furnace.—This furnace is employed in the duchy of Deux Ponts, where cinnabar or mercuric sulphide, associated with sandstone, is reduced by mixing it with about 25 per cent. of its weight of lime, and then distilling this mixture in earthen or cast-iron pear-shaped retorts; when double decomposition ensues with the production of calcic sulphide and sulphate which remain in the retorts, and the liberation of metallic mercury which distils over, thus—

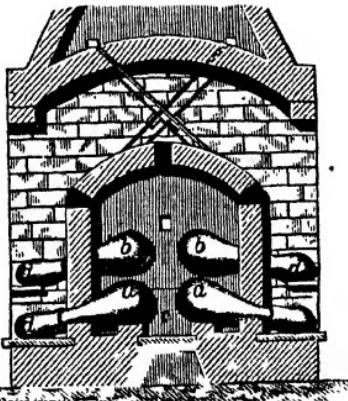


Fig. 47.—GALLERY FURNACE FOR
THE EXTRACTION OF MERCURY.



The gallery furnace, fig. 47, contains from 30 to 50 of these pear-shaped vessels or retorts, *a, a*, arranged in two rows, with their closed extremities towards the median line of the

furnace, and each row further contains two tiers, *a*, *b*, arranged one above the other, so that the flame and heated gases from the coal fire made on a grate, *c*, running the full length of the furnace between the two rows of retorts, but below and not in contact with them, passes upwards, around, and between the several retorts before escaping through the apertures shown in the arched roof of the gallery. Each of these retorts receives about 70 lbs. of the mixture of ore and lime (or if the ore be sufficiently calcareous in itself, then of the moistened ore alone), which charge occupies about two-thirds of the capacity of the vessel, at the same time the receivers *d*, *d* placed outside the gallery, and into which the necks of the retorts are received, are each half filled with water. As the distillation proceeds, the mercury is condensed by the water and collects in the bottom of the receivers, while the water itself becomes charged with a black powder known as *black mercury*, consisting of undecomposed sulphide and finely-divided mercury, which is collected, dried, and again distilled with a fresh portion of lime. When the charge of the retorts is exhausted, *i.e.*, has ceased to yield any metal, the contents of the several receivers are then emptied into a common receptacle or basin placed over another vessel put to receive the water as it overflows, whereby the mercury is collected in this basin and largely separated from the water, which overflows into the receiver below, carrying with it the whole of the *black mercury*.

Iron or iron scales can be equally well employed to effect the decomposition of the ore in this furnace, but no material performs this function more efficiently than lime. *

101. The Landsberg Process.—The method of treatment in the gallery furnace last described is obviously attended with loss of metal, and the expenditure of a considerable amount of manual labour in charging and recharging so many small retorts, with the luting of the several joints, etc., and to obviate this, at Landsberg in Bavaria, the apparatus illustrated in figs. 48 and 49 has been introduced; the ore, as in the last-mentioned process being reduced to a coarse powder and mixed with quicklime, is then introduced, in quantities of from 5 to 7 cwt., into each of the cast-iron retorts *a*, *a*, measuring about 7 feet in length, and arranged in groups of

three in each of the arched furnaces of brickwork, which are built several together. The charge is introduced from the back of the retort, the end being closed by a movable iron cover,

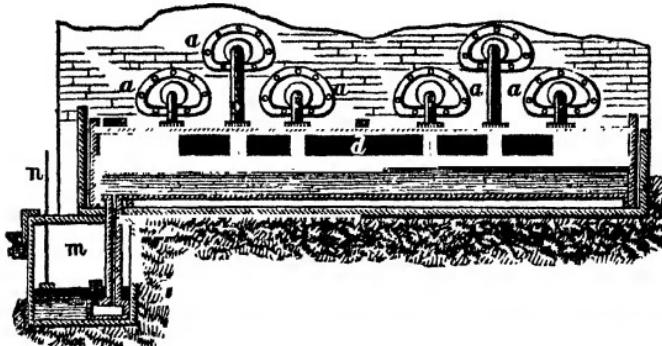
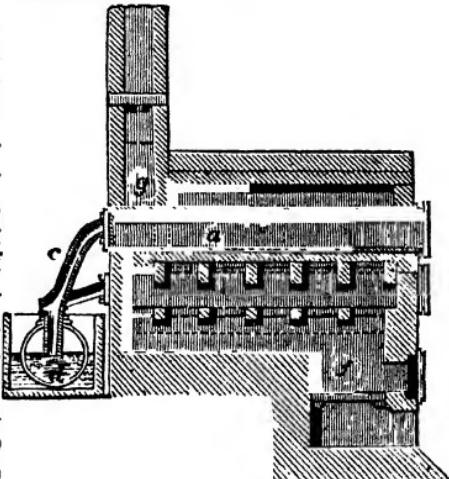


Fig. 48.—BAVARIAN FURNACE FOR THE TREATMENT OF ORES AND MERCURY.

while to the front extremity of each retort is attached a condensing pipe *c*, dipping beneath the surface of water contained in the slightly inclined main or pipe *d*, the last mentioned being kept cool by a current of water continually circulating around it; and the pipe *d* conveys the mercury from the whole of the retorts to a locked cistern *m*, in which the float *n* serves to indicate

the height of mercury collected. The retorts Fig. 49.—SECTION THROUGH ONE OF THE RETORTS OF THE BAVARIAN FURNACE. and the main *d* are each provided with safety valves to prevent accident by the sudden expansion or contraction of the air or vapours within the retorts. The retorts are built in masonry in the manner shown, after the manner of ordinary



gas retorts; the fireplace *f*, at one extremity, being situated beneath the central retort, which is protected from the direct action of the flame by fire-tiles; while a system of flues directs the gaseous current under and around each retort before it passes by the exit flue *g* to the stack, of which one serves for three furnaces or nine retorts. In working this furnace the temperature is maintained as uniformly as possible at a red heat, avoiding any sudden changes which might crack the retorts, etc., each charge being in this manner worked off in about three hours.

A variety of this retort, fitted with conical vertical receivers cooled by water running over their outer surface, is in use in certain parts of California for the treatment of the richer ores occurring there.

102. Reduction with Iron.—At Horzowitz, in Bohemia, this iron reduction method is pursued, the ore being mixed with smithy scales, and the mixture placed in iron dishes arranged one above another upon a vertical axis beneath an iron bell, the lower edge of which dips beneath the surface of water; fuel is then placed around the exterior of the bell constituting the furnace, when the heat produced is sufficient to effect the decomposition of the ore, and to distil the mercury which condenses and collects in the water in which the apparatus stands.

PURIFICATION OF COMMERCIAL MERCURY.

Commercial mercury is, as already noted, frequently contaminated with *zinc*, *bismuth*, *antimony*, *tin*, and other impurities; the two first mentioned being derived from their ores which are sometimes associated with the ores of mercury, and these metals being volatile like the mercury, they distil over along with, and are then dissolved in it, while the other metals mentioned are also soluble in mercury, and are sometimes added as adulterations; but since for many scientific and other applications to which mercury is applied, it is required to be perfectly pure, various methods have accordingly been applied for the separation of these several impurities.

As observed above, the operation of simple redistillation will not suffice to separate it from the volatile metals, zinc and bismuth; but if the surface of the metal contained in the

retort (of glass if for small operations, and earthenware or wrought iron, if upon a large scale) be covered with a layer of clean iron filings or turnings to the extent of about one-sixth the weight of the mercury, and the vessel then carefully heated by well bedding it in a sand bath, while the stout paper or canvas extremity of the neck or pipe from the retort is made to dip beneath the surface of water in the receiver, the latter being still further cooled by placing it in a large vessel also filled with water, or through which water circulates, then the heat of the bath is sufficient to boil the mercury, which distils over and is condensed in the water, while the other metals are retained by the layer of iron filings; but the mercury in the receiver, after pouring off the water, is yet generally covered with a thin film of oxide, with traces of ferric oxide, but these are readily removed by treating it with a little hydrochloric acid, after which the mercury is well washed and dried at a gentle heat.

Instead of the method of purification by *iron*, it is better to substitute for the latter coarsely-powdered *cinnabar*, which is added to the extent of about one-tenth the weight of the mercury, and the redistillation then proceeded with; in this manner the cinnabar suffers decomposition with the liberation of its mercury, while the foreign metals are largely converted at the same time into sulphides which remain in the retorts. Another method is to make the redistillation with the addition of a mixture of vermillion (the sublimed mercuric sulphide) or mercuric chloride with half their weight of lime; or the same effect is produced by redistilling the metal with mercuric oxide.

In lieu of the above *dry methods* of purification various *wet methods* are proposed, and amongst the most important reagents employed for the purpose may be noted *sulphuric* or *nitric acid*, and a solution of *mercurous nitrate*; but these methods obviously will not effect the removal of gold, silver, platinum, or other metal insoluble in these menstrums, but recourse must then be had to distillation to effect their elimination. If *sulphuric acid* be employed, then to the mercury contained in a flask or other vessel is added an equal weight of the concentrated acid, and the mixture is repeatedly stirred or shaken, when the action continues for several hours, or is

even prolonged in some cases to from five or seven days, the addition of fresh acid being made at intervals, so long as sulphurous anhydride continues to be evolved, or the acid continues to become turbid, since these actions only arise from the solution of foreign metals in the acid, pure mercury not being attacked by mere digestion with sulphuric acid in the cold.

If *nitric acid* be employed to effect the desired elimination, then the mercury is digested for some hours with the acid diluted with from 6 to 8 parts of water; the mixture of acid and metal being contained in a flat bottomed dish or basin, and maintained at a temperature of about 55°C. (131°F.), with frequent stirring or agitation of the mixture. The acid in this manner dissolves out most of the foreign and more readily oxidizable matters, while very little of the mercury is dissolved. When all action has ceased, the solution is decanted from the purified metal, and the latter requires only to be washed and dried.

When *mercurous nitrate* is substituted for the acids, then the mercury requires to be boiled for some hours with the mercurous nitrate dissolved in a small quantity of water.

Other methods of purification consist in agitating the metal with a solution of ferric chloride (*Ulex*); and an old method of Dr. Priestley, frequently adopted on the small scale, is to shake in a bottle a small quantity of the metal along with a little powdered loaf sugar, whereby the mercury becomes finely divided, and the foreign metals, as lead, etc., are exposed to the oxidizing influence of the air, which separate thereby as a grey powder, which is then separated from the metal by filtration through a cone of paper having a small aperture at the bottom, so that the mercury filters through, while the sugar retaining the foreign oxides remains in the cone.

CHAPTER V.

SILVER.

103. Physical and Chemical Qualities. — This metal is remarkable for its pure metallic whiteness, the rare metal *iridium*, although classed as a white metal, being inferior to silver in this respect; and Foucault states that the light transmitted through silver leaf is of a bluish or bluish-green colour. Silver has a very powerful metallic lustre, and in malleability and ductility it is only exceeded by gold, silver admitting of being hammered into leaves of not more than $\frac{1}{100000}$ th of an inch in thickness; but by hammering and wire-drawing, the metal becomes more or less brittle, and requires more frequent annealing than gold under the same conditions; while in hardness it stands between gold and copper, the hardness of gold, silver, and copper being as 4 to 5 to 7·2, the hardness of silver increasing, however, with the presence of any impurity in the metal.

The specific gravity of silver in the cast state is 10·53, which is increased under the coining press to 10·57, and in the finely divided state, as obtained by precipitation, its specific gravity is 10·62. This metal is possessed of considerable tenacity, a wire 1 sq. m.m. in diameter requiring at 0°C. a weight of 62·12 lbs. to break it, and if heated to 100°C. then 51·3 lbs. suffices, while at 200°C. the same wire broke under a load of 40·96 lbs. avoirdupois. It melts at a white heat, or at a temperature estimated by Pouillet at 1000°C. (1832°F.), and by Morveau at 1034°C. (1893·2°F.), its latent heat of fusion is 21·07°C., and specific heat between 0°C. and 100°C. is ·05701, while its dilatation per unit of length is ·000020826. At very high temperatures, as in the Voltaic arc, the metal is slightly volatilised, its vapour in the oxyhydrogen blow-pipe being of a pale blue colour inclining to purple.

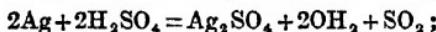
Silver, when occurring in crystalline forms, crystallises in

the regular system usually as cubes. It is one of the best conductors of both heat and electricity, is not acted upon under ordinary conditions by exposure to the air at any temperature, the tarnished surface so rapidly formed on articles of silver exposed to the atmosphere being usually due to a film of argentic sulphide formed on the surface, owing to the presence of traces of sulphuretted hydrogen in the air; but if the metal be kept in a state of fusion for a considerable time in contact with the air or oxygen, it is capable of absorbing about 22 times its own volume of oxygen, which it again liberates at the moment of solidification of the metal, the evolution being attended with the projection of the metal into a number of protuberances or craters on the surface of the silver, constituting the phenomenon of *spitting* or *vegetation*; but the presence of small quantities of copper prevents this absorption and spitting of silver, while perfectly pure silver, if heated to redness, absorbs and retains when cold $\cdot 545$ of its volume of oxygen, the metal thus affording an example of what is known as the "*occlusion*" of gases. But if pure silver be melted beneath a layer of 3 or 4 inches of common salt (NaCl) or potash, the metal sets with a clear bright surface, showing that oxygen was not absorbed and evolved again on solidification under these conditions; while if nitrate of potash or soda be substituted for the sodic chloride (NaCl), the same phenomena of *spitting* recurs, and by suitably heating with nitre the metal acquires the ornamental rough dead surface known as "*frosted silver*." Silver alloyed with as much as one-third of its weight of gold, still retains the power of absorbing oxygen and spitting on cooling, but larger proportions of gold prevent the action (Percy); and further, if silver wire be heated and cooled in hydrogen it occludes $\cdot 211$ of its volume of the gas. Silver melted on charcoal in a jet of oxygen burns with a conical flame, with the production of argentic oxide (Vanquelin), and also if heated in the air, by the passage of the electric spark, oxidation ensues.

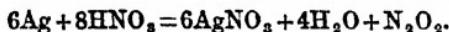
Water is without action upon silver at ordinary temperatures, but there is a notable disengagement of hydrogen if steam be passed over silver heated to whiteness, when the metal also spits during cooling. Silver, in a fine state of divi-

sion, when heated with cupric, plumbic, or manganic oxides, or with arsenic or antimony, is oxidized, the oxide produced remaining mixed with the excess of the other oxides, or in combination with arsenic or antimonite oxide, if either of these metals be employed; and thus although the oxide of silver cannot exist alone at the temperature here employed, yet, in conjunction with these oxides, the argentic oxide resists resolution into its elements.

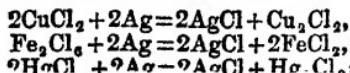
Silver decomposes sulphuretted hydrogen at the ordinary temperature, the metal becoming coated thereby with a brown or black film of sulphide of silver, the ornamental articles of what is known as *oxidized silver* are tarnished by a thin film of sulphide of silver, produced by boiling the article in a solution of potassic sulphide, and then removing the brown colouration from the prominent parts by brushing or wiping over them, whereby the tarnish or colouration is removed from such parts, and they appear with the lustre of silver. Silver combines with *chlorine*, *bromine*, and *iodine*, at the ordinary temperature; dilute *sulphuric acid* does not act upon the metal, but the stronger acid is decomposed when heated along with it, yielding sulphurous anhydride (SO_2) and argentic sulphate, according to the following equation—



and *hydrochloric acid* has little or no action upon the metal unless boiled with the finely-divided silver; but hydrochloric acid gas is decomposed by silver at a red heat, with the formation of argentic chloride and the liberation of hydrogen; while *nitric acid* is its best solvent, dissolving silver at the ordinary temperature, with the liberation of nitric oxide (N_2O_2), and the formation of argentic nitrate (AgNO_3)—



Alkaline chlorides convert metallic silver into chloride, which is dissolved in an excess of the alkaline solution; while cupric, ferric, and mercuric chlorides are reduced by silver to cuprous, ferrous, and mercurous chlorides respectively, according to the following equations—



and silver kept fused, and in contact with sodic chloride, (NaCl) suffers a loss in weight; while, if the metal be heated to bright redness, in contact with common salt, and with access of the air, argentic chloride is formed. The atomic weight of silver is 108, and its symbol is Ag .

104. Oxides of Silver.—Silver forms three oxides, known respectively as argentous oxide (Ag_4O), argentic oxide (Ag_2O), and argentic peroxide (Ag_2O_2).

Argentous oxide (Ag_4O) is prepared by heating argentic mellate, oxalate or citrate to a temperature of 100°C . (212°F .) in a current of hydrogen, when brown salts of this oxide are produced, which are dissolved in water, and from which solution argentous oxide is precipitated as a black powder on the addition of caustic potash.

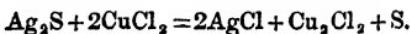
Argentic oxide (Ag_2O) is the salifiable oxide of silver; it is prepared by heating argentic carbonate to a temperature of 200°C . (424°F .), or it may be precipitated as a brown powder, becoming black on drying, by the addition of argentic nitrate to a hot saturated solution of baric hydrate. Argentic oxide, freshly precipitated from any of its solutions, rapidly absorbs carbonic anhydride from the air; it gives off the whole of its oxygen if heated below redness, and is completely reduced by carbon at a temperature below that at which it gives off its oxygen when heated alone. It is soluble in alkaline cyanides, hyposulphites, etc., but not in potash or soda, and by treatment with ammonia it yields the explosive compound known as "*fulminating silver*." Aqueous hypochlorous acid converts this oxide into argentic chloride, with the evolution of oxygen; chlorine gas likewise decomposes this oxide at the ordinary temperature, with the formation of argentic chloride and the liberation of oxygen.

Argentic peroxide (Ag_2O_2) is obtained by the electrolysis of a solution of argentic nitrate, when this oxide is deposited in the form of black acicular crystals on the positive pole.

105. Argentic Sulphide (Ag_2S).—This is the only compound of sulphur with silver; it occurs native as *silver glance*, or vitreous argentic sulphide, and may be prepared artificially by heating silver with an excess of sulphur, when combination, accompanied by incandescence, occurs at a temperature of redness; the resulting sulphid, not acting so corrosively

upon the material of the crucible as occurs with the corresponding lead compound; metallic silver also decomposes sulphuretted hydrogen at the ordinary temperature, with the production of argentic sulphide; and this sulphide is also precipitated from the solutions of silver salts on the addition of sulphuretted hydrogen. The artificial sulphide, after fusion, is of a lead or dark-grey colour, feebly metallic in appearance, is somewhat malleable, and so soft that it may be cut with a knife. The specific gravity of the artificial product is 6·85 (Karsten), and of the native variety from 7·196 to 7·365, the latter crystallising in the regular or cubic system. Argentic sulphide is practically fixed, if heated with the exclusion of air, even at a high temperature. It is not oxidized by exposure to the air, but if heated with access of the air it is slowly decomposed, yielding sulphurous anhydride and metallic silver; but if ignited in hydrogen or steam it is largely decomposed, and if the latter be employed the silver remains in hair-like threads, resembling native silver. This sulphide is insoluble in water, ammonia, or ammonic carbonate, in potash, soda, sodic sulphate, potassic cyanide, and potassic or sodic carbonate; it is attacked by chlorine when heated with the gas, chloride of sulphur being evolved, and if the temperature be high enough, argentic chloride remains; dilute hydrochloric acid is without action upon the sulphide, but the stronger acid attacks it, the sulphide becoming coated, however, with a layer of argentic chloride, which prevents the further action of the acid.

Metallic silver fused along with argentic sulphide retains a certain proportion of the latter, and the fused sulphide is decomposed by iron; but if the argentic sulphide contain also cupreous sulphide, complete separation of the silver cannot be effected in this manner. Lead and copper act in a similar manner to iron, but less perfectly. Argentic sulphide in the presence of common salt, air, and moisture, yields argentic chloride; also, this sulphide when treated with cupric chloride yields argentic chloride, cupreous chloride, and sulphur, thus:



And the cupreous chloride so formed will, with access of air, produce a greenish deposit of an oxychloride of copper, and

it is upon this reaction that depends the preliminary treatment of the ore (argentic sulphide) in the Mexican amalgamation process for the extraction of silver.

106. Argentic Sulphate (Ag_2SO_4).—This salt is prepared by treating grain silver, or silver filings, with strong boiling sulphuric acid; it forms a colourless, anhydrous, and inodorous body, crystallising in the prismatic system; only sparingly soluble in water, but more soluble in dilute sulphuric acid. Its specific gravity is 1.25. At a strong red heat it is decomposed into sulphurous anhydride and oxygen, which escape, and a residue of metallic silver; and if treated with carbon at a red heat the metal is reduced, while sulphurous anhydride (SO_2) and carbonic anhydride (CO_2) in equal volumes are given off. Silver is precipitated from solutions of this salt by metallic copper.

The liquor known as "*stripping liquor*," employed for dissolving the silver from old plated articles, consists of 3 lbs. of sulphuric acid diluted with 1 lb. of water, and containing in solution $1\frac{1}{2}$ oz. of nitre, the liquid being used at a temperature of from 38°C . (100°F .) to 93.3°C . (200°F .), when the silver dissolved by this liquor is then precipitated as chloride by the addition of common salt.

107. Argentic Sulphite (Ag_2SO_3).—This is a colourless salt prepared by adding sodic sulphite (Na_2SO_3) or sulphurous anhydride to a soluble salt of silver; it is only slightly soluble in water, and undergoes no change from exposure to the light. If heated to 200°C . (392°F .) with water, it is decomposed, yielding argentic sulphate and metallic silver. It forms double salts with alkaline sulphites.

108. Argentic Hyposulphite ($\text{Ag}_2\text{S}_2\text{O}_3$).—This is an exceedingly unstable compound, but it forms two series of double hyposulphites with the alkaline hyposulphites: thus argentic oxide, bromide, and chloride are completely dissolved in sodic-hyposulphite, with the formation of a sodio-argentic hyposulphite of the formula $\text{Na}_4\text{Ag}_2\text{S}_6\text{O}_9$. The silver in these hyposulphites can only be detected by hydrochloric acid on heating the solution, and adding the acid occasionally, when argentic chloride is precipitated in a form readily freed by washing from the other salts.

109. Argentic Nitrate (AgNO_3).—This salt constitutes,

when fused, the "*lunar caustic*" of the surgeon. It is obtained on the solution of silver in nitric acid, from which solution it crystallises in colourless anhydrous crystals, belonging to the trimetric or prismatic system; it is soluble in water, yielding a neutral solution. This salt melts at 219° C. (426° F.); in contact with organic matter, or on exposure to sunlight it rapidly blackens, from the reduction of metallic silver. Lead, tin, cadmium, copper, antimony, and mercury, separate silver from aqueous solutions of this salt. *Phosphorus* has a like effect; and carbon, also if immersed in its solution, slowly reduces the metal—a reaction presumed to be due to the presence of hydrogen in the carbon; and the salt also suffers decomposition by fusion in an iron vessel. Argentie nitrate is frequently adulterated in commerce by plumbic, potassic, and sodic nitrates. In the preparation of argentie nitrate by the solution of silver in nitric acid, if the silver contain also copper, this passes into solution, imparting, if in quantity, a greenish tint to the solution; and to separate which, hydrochloric acid is added, by which the silver is precipitated as argentie chloride, which is separated and well washed; when after digestion of the washed precipitate with a solution of potash, by which it is converted into argentous oxide (Ag_2O), it is then again washed to free from potash and dissolved in nitric acid, by which means the pure salt is obtained.

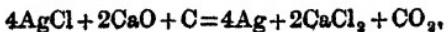
110. Chlorides of Silver.—Silver and chlorine exert powerful chemical affinities for each other, combining with one another at ordinary temperatures, and by their union yielding two chlorides known respectively as argentie chloride (AgCl) and argentous chloride (Ag_2Cl).

Argentie chloride (AgCl) occurs native as *horn silver*, in waxy masses or crystallised in different forms of the cubic system; the same chloride is also precipitated as a white curdy precipitate when hydrochloric acid or a soluble chloride is added to a soluble salt of silver (except the hyposulphite), water containing but $\frac{1}{113000000}$ th of hydrochloric acid becoming turbid on the addition of a solution of argentie nitrate; this chloride also results when chlorine or hypochlorous acid is passed over heated silver, or on passing hydrochloric acid over silver heated to redness. Argentie chloride is partially

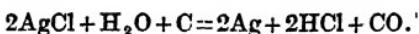
decomposed by exposure to sunlight, with the separation of chlorine and the formation of a dark-grey or nearly black argentous chloride (Ag_2Cl). The amorphous chloride has a specific gravity of 5.501, which after fusion becomes 5.548. At a temperature of about $260^\circ\text{C}.$ ($500^\circ\text{F}.$), argentic chloride melts to a thin yellow liquid, which solidifies on cooling to a translucent waxy mass, resembling horn silver in appearance, and which, when cooled in mass, may be turned in the lathe. Argentic chloride is volatile at a strong red heat, and is insoluble in water, nitric acid, sulphuric acid, or dilute hydrochloric acid; it is, however, soluble in 200 parts of strong hydrochloric acid, or in 600 parts of the same diluted with twice its amount of water, but is again deposited on cooling or evaporating; while by boiling with sulphuric acid, the chloride suffers decomposition. Argentic chloride is also readily soluble in ammonia, from which solution the silver is precipitated as argentic sulphide (Ag_2S) on the addition of sulphuretted hydrogen; it is soluble in hot solutions of sodic chloride and in sodium hyposulphite, potassic or sodic cyanide, as also in a solution of tartaric acid, in a cold solution of mercurous nitrate, and in the soluble sulphites. Argentic chloride is readily decomposed by heating in a current of hydrogen, the reaction being accompanied by the evolution of hydrochloric acid, and the separation of metallic silver; weak alkaline solutions do not affect argentic chloride, but by boiling the freshly precipitated chloride with a solution of potash, having a specific gravity of at least 1.25, and continually stirring, then potassic chloride and black oxide of silver (Ag_2O) are produced, this constituting Gregory's process for the preparation of the latter. In the presence of organic matters, as cane or grape sugar, glucose, etc., argentic chloride is reduced to the metallic state, and the chloride is also reduced by fusion with sodic or potassic carbonates, with the elimination of oxygen and carbonic anhydride; thus—



and by heating to the melting point of silver with lime and carbon, the metal is again reduced,



Also at a white heat charcoal and steam effect the same reduction; thus—



Zinc or iron in contact with water separates metallic silver from argentic chloride, the reaction being much promoted by acidifying the water with hydrochloric acid, and the injection of steam; it is also reduced by tin, antimony, lead, bismuth, and copper. Argentic chloride, heated in a current of carbonic oxide, yields metallic silver and carbonic dichloride (COCl_2); it is also decomposed in small proportions if heated with sulphur, with the formation of a sulpho-chloride of silver. Plumbic sulphide, and probably other sulphides melt and combine with argentic chloride; while litharge (PbO) melts in all proportions with argentic chloride, and if plumbic sulphide be added to the melted mixture, metallic silver is reduced. Argentic chloride is reduced by powdered resin, this constituting the *dry method* devised by Mohr for the preparation of fine silver, in which argentic chloride is mixed with one-third of its weight of powdered resin; the mixture being introduced into a crucible and heat applied, at first gently, and subsequently sufficiently strong to melt the silver, the reducing agent in this reduction being the hydrogen of the resin.

Argentous chloride (Ag_2Cl) is obtained by treating argentous oxide with hydrochloric acid, or by precipitating a soluble argentous salt with chloride of sodium, or, as already stated, it results on the exposure of argentic chloride to sunlight. This salt is resolved into argentic chloride (AgCl) and metallic silver if heated to the melting point of argentic chloride.

111. Argentic Iodide.—This compound occurs native, but may be prepared artificially by treating silver filings with iodine, or may be precipitated by the addition of a soluble iodide to argentic nitrate. As precipitated by an excess of potassic iodide (KI), it forms a pale yellow compound sensibly affected by exposure to sunlight; while if the argentic nitrate be in excess, the precipitate is darker in colour, becoming pale-grey, and eventually black on exposure to sunlight. Argentic iodide (AgI) is insoluble in water, scarcely soluble in am-

monia, and is insoluble in cold solutions of alkaline chlorides, while sodic-hyposulphite dissolves it readily. It is decomposed, like the chloride, by the action of zinc, etc., in acidified water; it is not decomposed by dilute nitric acid; but, if heated with strong nitric or sulphuric acid, it suffers decomposition with the separation of free iodine.

112. Argentic Bromide.—Argentic bromide occurs *native* as *Bromargyrite*, a mineral of a greenish-yellow colour, with considerable lustre; it is also precipitated as a yellowish-white precipitate when potassic bromide is added to a solution of argentic nitrate, while bromine and silver in a fine state of division combine at ordinary temperatures. This compound is only slightly acted upon by exposure to daylight; it melts below a red heat with the production of a reddish fluid, which forms a yellowish, horny-looking mass on cooling; it is insoluble in water, is soluble in ammonia, though not so readily as the chloride, and is readily soluble in sodic-hyposulphite or potassic cyanide.

113. Argentic Phosphide.—Phosphorus and silver unite at a red heat. If phosphorus be placed upon silver heated to redness, the whole fuses, the silver taking up phosphorus, a portion of which is again separated as the fused mass solidifies (Pelletier). This compound is also formed by fusing silver with glacial phosphoric acid and charcoal, or by heating finely-divided silver in the vapour of phosphorus. Phosphuretted hydrogen precipitates silver in a fine state of division when passed into a solution of argentic nitrate (Rose).

114. Alloys of Silver.—The presence of only small quantities of *arsenic* in silver renders the latter brittle and liable to crack when rolled, though this metal is not so destructive of the malleability of silver as it is in the cases of gold or copper.

Silver and copper combine when melted together in any proportion, the resulting alloys being comparatively homogeneous, though ingots of the alloy are not absolutely identical in composition throughout; but in such as contain from 50 to 300 parts of copper per 1000 the interior of the ingot is usually the richest in silver, while if the copper form from 300 to 900 parts per 1000, then the exterior of the ingot is the most highly argentiferous, and the alloy containing

28.107 per cent. of copper and 71.893 per cent. of silver gives an almost perfectly homogeneous alloy (Levol). These alloys are white in colour until the copper amounts to 50 per cent. of the alloy, while the tint becomes more and more red with the increase in the amount of copper above this limit. The effect of copper is to *increase the hardness and elasticity* of the alloy, the hardest mixture consisting of about 5 parts of silver to 11 of copper; the *ductility* of these alloys is considerable, but still inferior to pure silver, while their *specific gravity* is less than the mean of the metals employed in their preparation. When heated in a muffle or other oxidizing atmosphere, the alloys of these metals are superficially oxidized, with the production of variously-coloured films on the surface, according to which a crude estimate of the amount of copper in the alloys may be determined; thus *pure silver*, when heated in the muffle, becomes *dull white* in colour, while if alloyed with 50 parts of copper per 1000 it becomes *dull greyish-white*; with 100 parts of copper per 1000 it assumes a *dull greyish-white* colour with *black* fringes along the edges; while with 120 to 140 parts of copper per 1000 the alloy becomes *grey* and almost *black*; and if the copper reach 160 parts per 1000 of the alloy it is rendered quite *black* by the treatment. Silver does not oxidize on the application of heat; but on heating the highly cupriferous alloys of silver both metals are oxidized, and also on heating such a body with sulphur both metals combine with this element, although the copper does so in the largest proportion.

The chief and most important applications of the alloys of silver and copper are for the purposes of *coinage* and for the manufacture of ornaments, cutlery, etc., for which uses pure silver is too soft to withstand the necessary wear, and it is hence alloyed with copper to obtain the required hardness. The British silver coinage contains 11 oz. 2 dwts. of *fine* silver and 18 dwts. of copper per lb. Troy; or it contains 925 parts of silver per 1000, which standard was introduced by Edward I. This alloy has a specific gravity of 10.3, and is designated *sterling* or *standard* silver, the *English standard* thus containing 925 parts of *fine* silver per 1000, or contains 18 dwts. of copper per Troy lb.; and in commerce the purity

of silver is referred to this standard, reports upon other specimens being made in terms of *pennyweights better or worse* than the standard. Thus the French coinage, which contains 24 dwts. of copper per lb. Troy, is thus stated to be *worse* 6 dwts. ($24 - 18 = 6$); while the Indian rupee contains only 12 dwts. of copper in the Troy lb., and would accordingly be described as *better* 6 dwts. The French have three standard alloys, that employed for coinage containing 900 parts of silver per 1000; a second containing 950 parts of silver per 1000 is employed for medals and plate, while the third, containing only 800 parts of silver per 1000, is employed for jewellery. Messrs. Elliot & Storer have detected considerable proportions of lead in the coinage of different countries; thus an English shilling dated 1816 contained .484 per cent. of lead, and a five franc piece, dated 1852, contained .428 per cent. of lead.

In England all sterling silver goods are marked at offices appointed for that purpose with what is known as the "*Hall Mark*," consisting of a *Lion passant*, indicating 11 oz. 2 dwts. of fine silver in the Troy lb.; or by *Britannia* if containing 11 oz. 10 dwts. of silver per Troy lb.; in addition the place of manufacture is denoted by heraldic arms, the year by a letter used throughout that year, and changed from year to year; and lastly with the Queen's head, indicating that the duty has been paid. Of the heraldic arms employed to indicate the place of manufacture, London is indicated by a Leopard's Head, Birmingham by an Anchor, Chester by a Sword between three Wheatsheaves, Sheffield by a Crown, and Exeter by a Castle with three Towers.

Gold and silver occur native alloyed in various proportions; and artificial homogeneous alloys of these metals may be formed in almost all proportions. All *native* gold contains more or less silver.

Lead and silver may be melted together in almost all proportions, with the production of apparently homogeneous alloys, except in large masses, which, when cooled slowly, are not uniform throughout; the interior of the mass being more highly argentiferous than the exterior. Lead impairs the malleability of silver, and the alloys of these two metals have no direct application in the arts.

Mercury slowly dissolves silver at the ordinary temperature, but much more rapidly and perfectly on the application of a gentle heat; and in either case the combination is attended with considerable contraction in volume, and the production of a soft, granular, or crystalline white amalgam, readily miscible with an excess of mercury, but which excess can be separated from the pasty amalgam by squeezing it through wash-leather. These amalgams if heated to redness give off their mercury, the silver retaining, however, sometimes traces of mercury. A native amalgam of mercury and silver occurs crystallised in the Palatinate, in Dauphiné, Hungary, Sweden, Spain, Chili, etc.

Nickel, when alloyed with silver, yields hard, greyish-white, and magnetic alloys. Such an alloy, containing 10 per cent. of nickel, constitutes the Swiss coinage.

An alloy containing 4 parts of silver to 1 of *zinc* constitutes Döppler's reflector metal. The alloys of these metals have a bluish-white colour.

Palladium and silver combine in almost all proportions, with the production of alloys capable of receiving a fine polish, and which were formerly employed for the graduated and polished scales of philosophical instruments.

115. Ores of Silver.—Owing to the comparatively high value of silver, and the facility with which it is extracted from the ores or minerals containing it, the separation of silver is rendered profitable although the mineral contains but an exceedingly small percentage of the metal; and thus, while certain of the silver ores in their pure state contain a very high percentage of the metal, yet the ores usually treated in the smelting-works of Europe and America contain only a small proportion of silver. Thus the Mexican ores contain on an average but .25 per cent. of silver, and are considered rich if the proportion of silver attain to .5 per cent.; and in Europe the ores worked at Clansthal in the Hartz contain only about .098 per cent. of silver on the average; while at Freiberg ores containing but .05 per cent. of silver may be profitably worked; and further, if the ore contain upwards of 35 per cent. of lead or 5 per cent. of copper, the silver is extracted, if it form not more than .01 per cent. of the ore. The ores of Joachimsthal, which average the richest in

Europe, generally contain from 2 to 3 per cent. of silver, and rarely exceed 10 per cent. (Lamborn).

Silver occurs in the native state, in combination with sulphur, chlorine, bromine, and iodine, as also in combination with other metals, as arsenic, antimony, etc., and with mercury as a native amalgam, whilst also frequently occurring in minerals essentially ores of other metals, occurring thus in ores of lead, copper, zinc, etc., constituting argentiferous galena, grey copper ores, blonde, etc. This latter class of ores frequently containing, as above stated, sufficient silver to render its extraction profitable, when such minerals are also considered as ores of silver. The ores of silver occur in veins traversing gneiss, granite, clay-slate, quartz, calc-spar, micaschist, etc., and are usually associated with ores of lead and copper, blonde (ZnS), spathic iron ore, brown haematite, pyrites, ores of nickel and cobalt, heavy-spar, quartz, earthy carbonates, etc. The ores of silver are more or less abundantly distributed over all parts of the world; and the metal has thus been worked in Peru, Chili, Colorado, Nevada, Mexico, United States, and other parts of the American continent; in Norway, Sweden, Saxony, Hungary, Transylvania, Brittany, Spain, etc., etc.

Native silver is rarely found perfectly pure, but usually contains also gold, copper, platinum, or other metals in larger or smaller proportion, and is itself always present in small quantities in native gold. Native silver occurs in laminated or filamentous masses, or capillary and in grains minutely disseminated through silver ores and other minerals; occasionally also massive, or crystallised in cubes and other forms of the regular system. It has a silver-white colour and streak, a metallic lustre, and a specific gravity of from 10·1 to 11·1, with a hardness of from 2·5 to 3. Native silver is often associated with iron in ferruginous rocks, as in Mexico, Peru, and Chili, and with native copper, as in the Lake Superior district of North America; it also occurs in Peru, Kongsberg in Norway, in the Hartz, the Urals, Freiberg in Saxony, and Schemnitz in Hungary.

Silver-glance, or vitreous argentic sulphide (Ag_2S), sometimes occurs crystallised in cubes, octahedrons, and other monometric forms, but more frequently in the massive state.

This mineral has a dark lead-grey colour, with a metallic or glassy lustre, a conchoidal or uneven fracture, and may be cut with a knife, having a hardness of about 2·5. It possesses a certain amount of malleability and elasticity; is fusible at the temperature of an ordinary flame, and its specific gravity ranges between 7·196 and 7·365. The pure sulphide contains 87·1 per cent. of silver, but it rarely occurs pure as an ore, being often associated with the sulphides of lead, copper, iron, zinc, antimony, arsenic, and tin, or with the ores of nickel and cobalt; so that the ore containing this mineral as its source of silver, yields much smaller proportions of silver than the pure sulphide. Silver-gleance constitutes one of the richest, most abundant, and usual forms of occurrence of silver, occurring in veins, and sometimes in large masses, in the Hartz, Saxony, Bohemia, Norway, Hungary, Mexico, Peru, Chili, Nevada, Siberia, etc.

Brittle silver-gleance, stephanite, brittle silver ore, etc., are names applied to a sulphantimonite of silver ($5\text{Ag}_2\text{S}\text{Sb}_2\text{S}_3$) forming a valuable ore of silver containing, when pure, 71 per cent. of this metal. It occurs massive, compact, disseminated or crystallised in trimetric forms, possessing a black or iron-grey colour and streak, with a metallic lustre, a hardness of from 2 to 2·5, specific gravity 6·299, and an uneven fracture. It decrepitates and fuses readily on charcoal before the blowpipe, evolving fumes of antimony and sometimes also of arsenic, and yields a button of metallic silver. This ore accompanies other ores of silver at Freiberg, Schneeburg, etc., in Saxony; Schemnitz in Bohemia; Kremnitz in Hungary; Andreasberg in the Hartz; and in Mexico, Peru, Chili, Nevada, etc.

Argentiferous copper-gleance, Stromeyerite or sulphide of silver and copper ($\text{Ag}_2\text{S}\text{Cu}_2\text{S}$), is a mineral of a dark steel-grey colour, with a shining streak, a hardness of from 2·5 to 3, and specific gravity of from 6·2 to 6·3. It occurs massive, as also crystallised in trimetric forms. The pure ore would contain 53·08 per cent. of silver, but it is usually more or less mixed with copper-gleance, and hence yields but from 3 per cent. to 30 per cent. of silver.

The mineral known as *Antimonial Silver* contains, when pure, 77 per cent. of the metal, and has a white colour and

streak, with a metallic lustre, an uneven fracture, a hardness of from 3·5 to 4, and specific gravity of from 9·4 to 9·8; it fuses readily, evolving antimonious fumes, and yielding a button of silver. It occurs in the Hartz, Dauphiné, South America, etc.

Pyrargyrite, dark red silver ore, or ruby silver, has a composition represented by $3\text{Ag}_2\text{S}\text{Sb}_2\text{S}_3$, and occurs massive, granular, or crystallised in forms of the prismatic system. It varies in colour between black and dark redness, with a red streak, is transparent or opaque, has an adamantine lustre, a hardness of from 2 to 2·5, and a specific gravity of from 5·7 to 5·9. This mineral occurs with calcite, galena, etc., in the Hartz, in Mexico, Chili, Saxony, Norway, Hungary, Spain, and also in Cornwall.

Proustite, or light red silver ore ($3\text{Ag}_2\text{S}\text{As}_2\text{S}_3$), much resembles the last in physical characters, occurring granular or crystallised in forms of the prismatic system, is subtranslucent, and possesses an adamantine lustre, with a cochineal red colour and streak. It has a hardness of from 2 to 2·5, and a specific gravity of from 5·422 to 5·56; it is soluble in nitric acid, and is analogous to pyrargyrite in composition, with the substitution of arsenic for the antimony in the latter. It is found in Saxony, Bohemia, Baden, Dauphiné, Spain, Mexico, Peru, and elsewhere.

Fahl-ores, *Fahlerz*, *Tetrahedrite*, are names applied to a class of minerals consisting of sulphantimonites and sulpharsenites of silver and copper, containing also iron, tin, lead, and mercury, and which are sometimes very rich in silver, containing occasionally as much as 1400 oz. of silver per ton of ore; but the more usual content of these ores is from 2 per cent. to 10 per cent. of silver. These ores occur granular, crystalline, compact, or crystallised in forms of the monometric or cubic system, and varying in colour between steel-grey and iron-black, with a streak usually of the same colour as the mineral, with a hardness between 3 and 4·5, and a specific gravity of from 4·5 to 5·1. A variety of fahlerz is known as *Polytellite*. These ores occur at Andreasberg in the Hartz, Kremnitz, in Hungary, Saxony, Sweden, Transylvania, South America, Cornwall, etc. *Freibergite* ($4\text{Ag}_2\text{S}\text{Sb}_2\text{S}_3$) is another variety of these fahl-ores.

Polybasite is a sulpharseno-antimonite of silver and copper, possessing an iron-black colour and streak, metallic lustre, a hardness of from 2 to 3, and a specific gravity of 6.214, which occurs massive, disseminated, or crystallised in the hexagonal system, in Saxony, Hungary, Cornwall, etc.

Horn-silver, or argentic chloride (AgCl), occurs as a soft, pearl-grey, or greenish-white, waxy, or horny-looking mass, which is translucent on the edges, and may be cut with the knife, its hardness being only from 1 to 1.5. It has a resinous lustre, a shining streak, and a specific gravity of from 5.4 to 5.5. It fuses in the flame of a candle, and is readily reduced to the metallic state on charcoal before the blowpipe. This compound is also found crystallised in cubes, octahedrons, and other monometric forms. Argentic chloride contains, when pure, 75.25 per cent. of silver, and occurs accompanying other silver ores somewhat abundantly in Peru, Chili, and Mexico, and less frequently in Saxony, Kongsberg, in the Hartz, Norway, Cornwall, etc.

Bromargyrite, or argentic bromide, is a mineral of a yellow or greenish colour, with a strong lustre; it is soft and sectile, with a specific gravity of from 5 to 6. It occurs accompanying argentic chloride in the mines of Mexico, Chili, etc.

Iodargyrite, or argentic iodide, is a soft, sectile, yellow, or yellowish-green translucent mineral, occurring in lamellar flexible plates, or crystals belonging to the hexagonal system, possessing a resinous lustre and yellow streak; it is readily fusible before the blowpipe, to the flame of which it imparts a red colour, and if conducted on charcoal, the silver is reduced. It contains, when pure, 46 per cent. of silver, and occurs in Mexico, Chili, Coquimbo, Spain, etc.

A compound of silver and mercury known as "*Amalgam*" occurs native, crystallised in cubes and other monometric forms, as also in the massive or amorphous state. It is a brittle body of a silver-white colour and streak, having a conchoidal fracture, a hardness of from 3 to 3.5, and varying in specific gravity from 10.5 to 14. This body has a very variable composition, for while some specimens agree with a formula of AgHg , others again have a composition represented by Ag_{12}Hg . It is found in the Palatinat, in

Dauphiné, in Hungary, Sweden, France, Spain, Chili, Atacama, Coquimbo, etc.

Of other minerals containing silver, and which are available as ores of silver when they occur in sufficient quantity, may be noted *Bronniardite* $2[\text{Pb},\text{Ag}_2]\text{S},\text{Sb}_2\text{S}_3$; argentic carbonate or *Selite* (Ag_2CO_3); *Telluric silver* (Ag_2Te); *Naumannite*, or argentic selenide (Ag_2Se); *Sternbergite* $3[\text{Fe};\text{Ag}]\text{S},\text{Fe}_2\text{S}_3$, or containing nearly equal proportions of silver, sulphur, and iron; *Polyargyrite*, containing antimony, sulphur, zinc, lead, iron, and silver; *Xanthocone*, a compound of silver, arsenic, and sulphur, containing 64 per cent. of silver when pure; *Miargyrite* ($\text{Ag}_2\text{S},\text{Sb}_2\text{S}_3$); *bismuthic silver* (AgBi). *Blende*, *iron pyrites*, *mispickel*, etc., occasionally contain sufficient silver to render its extraction profitable; while *argentiferous galena* is the subject of general treatment for silver, the facility with which the silver may be concentrated in the lead and subsequently separated by the process of *cupellation*, rendering its extraction profitable if it be present to the extent of not more than from 2 oz. to 3 oz. per ton of lead, and a similar remark extends to the extraction of silver from certain copper ores.

EXTRACTION OF SILVER FROM ITS ORES.

The great variety of processes still employed for the extraction of silver, in different parts of the world, and each one possessing advantages over the others for the treatment of the ores of particular localities, are rendered necessary by the great diversity existing in the associates of the metal, and also of the very large amount of materials that it is necessary to operate upon, owing to the argentiferous minerals often occurring minutely disseminated through large proportions of an earthy matrix or gangue, and in others more or less intimately mixed with ores or compounds of other metals, as galena, copper ores, etc. The methods employed for the separation of metallic silver from its ores, or metallurgic products in which it exists in notable quantity, may, however, be classed under three heads, viz.—

I. The different methods of *amalgamation* as employed in Mexico, Saxony, and elsewhere, based upon the solubility of

metallic silver in mercury, and the subsequent ready explosion of the latter on the application of heat to the amalgam. These methods include,

- 1°. The *Mexican methods of amalgamation in heaps*.
- 2°. The *European system of amalgamation in casks*, known also as the "barrel process."
- 3°. The methods of *amalgamation in kettles or pans*.

II. Various *wet methods*, for the extraction of silver from its sulphides by first converting them into chloride or sulphate, which is then dissolved out by water, solution of common salt, or other suitable solvent, and the silver subsequently deposited by precipitation from the solutions so obtained, these methods including—

- 1°. "*Augustin's*" method, by which the ore or cuprous regulus is converted into argentic chloride, which is then extracted by a solution of *sodic chloride*, and the silver afterwards precipitated by metallic copper.
- 2°. The method of "*Zier vogel*" for the conversion of argentic sulphide into *sulphate*, which is subsequently dissolved out by *hot water*, and the silver precipitated as cement silver as in the Augustin process.
- 3°. The method of "*Von Patera*," by which the argentic sulphide is converted into *chloride*, which is then dissolved out by a solution of *sodic hyposulphite*, from which the silver is reprecipitated as argentic sulphide freed from other metals, the sulphide being then reduced by the application of heat.

III. The methods in which the *silver is concentrated in a quantity of lead*, from which it is subsequently separated by the process of *cupellation*. The silver in argentiferous copper, copper matts, or other regulus, which was formerly separated by amalgamation methods, etc., is now separated by these methods, and very rich silver ores are also treated by these methods; while, in fact, *all* silver ores may be treated by fusion with *galena* or other lead-yielding product, with the separation of a larger proportion of silver than is effected by the amalgamation processes; but owing to the scarcity of fuel in certain localities, this method cannot be applied, and the methods of amalgamation are there accordingly more convenient and economical.

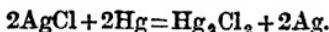
AMALGAMATION METHODS FOR THE EXTRACTION OF SILVER.

The amalgamation methods, though entailing a considerable waste of mercury as will subsequently appear, do not require the expenditure of much fuel, and the processes are therefore especially suitable to the requirements of countries like Mexico, Peru, etc., where *fuel and water are scarce, and means of transport expensive*. These methods are also adapted to the treatment of refractory ores and such as contain but small proportions of silver, while the operations involved are more simple, and the extraction of the metal is more rapid, than in smelting methods; but these (amalgamation) methods are not applicable to the treatment of ores containing any considerable proportion of lead or copper, since both of these metals are lost when the ore is treated by amalgamation; and further, the ores for amalgamation should be as free as possible from bismuth, nickel, and cobalt. Likewise the amalgamation methods are attended with a larger loss of gold in the case of auriferous silver ores than when such ores are treated by smelting processes. But the more modern and *wet methods* of Augustin and Zier vogel have, to a large extent, supplanted the amalgamation works in Europe.

116. Mexican Amalgamation Method.—Previous to the discovery of California, Mexico was the chief seat from whence we derived our supplies of silver, and the metal was wholly extracted by the amalgamation or “*Patio*” process. This method, invented by Bartholomé Medina about 1557, is, with only slight modifications, the method still pursued for the extraction of this metal in Mexico and other silver-yielding districts of America.

The ores of Mexico are chiefly sulphurous ores, accompanied by smaller quantities of native silver, by argentic chloride, bromide, and iodide, with some more complex combinations of silver with antimony and arsenic, the ore yielding on an average about 25 per cent. of silver. Before the argentic sulphide (Ag_2S), etc., can be acted upon by the mercury it is necessary to convert it into chloride or into metallic silver, so that the first portion of the process has for its object the conversion of argentic sulphide (Ag_2S) into argentic chloride (AgCl), which, on subsequent treat-

ment with mercury in the amalgamation, is resolved into mercurous chloride (calomel) and metallic silver thus—



The ores are first picked for the separation of the richer portions known as *colorados*, consisting of chloride, bromide, and iodide of silver, with native silver, from the portions containing silver in combination with sulphur, antimony, and arsenic; while a still poorer portion is separated and rejected as worthless. The richer portions are treated separately, and occasionally undergo a concentration by washing before treating for the extraction of the silver.

The sorted ore is then stamped under stamps usually driven by water or mule power, and then ground with water to a fine powder or mud in a grinding apparatus known as an "*arrastra*" or "*tahona*." The stamps resemble the Cornish stamps employed for breaking tin ores, the stamp-heads being of wrought iron, and weighing from 100 lbs. to 200 lbs. each, and are raised by cams on a shaft moved by water-power or driven by mules. Each stamping-mill contains 9 heads, giving 27 strokes per minute, with a fall of 22 inches, and the stamped ore falls on to a sieve formed by a strong hide perforated with numerous holes of about half an inch in diameter, which is stretched over a pit on each side of the stamps. The *arrastra*, fig. 50, is a shallow pit of from 9 to 12 feet in diameter, and about 1 foot deep, consisting of a circular bed of porphyry or other hard stone, set on end, smoothly dressed, and surrounded by a wooden tub. In the centre of the pit is pivotted a vertical shaft *a*, towards the lower extremity of which are attached four radial arms, to each of which is tied or attached by chains, a large mure or



Fig. 50.—ARRASTRA OR MEXICAN GRINDING APPARATUS.

less rectangular porphyritic stone *b*, by which the grinding is effected, the rotation of the vertical shaft, and with it of these stones, being effected by mules attached to the prolonged extremities of two of the arms, or to an independent one inserted for this purpose, the mules making from $3\frac{1}{2}$ to 4 revolutions per minute. The ore from the stamping-mills is treated in this mill with the addition of a little water from time to time, and the grinding continued until a very fine mud or powder is produced, each arrastra grinding about 10 quintals (1 quintal equals nearly 100 lbs. avoirdupois) of ore in the course of 15 hours. It is usual to place several of these arrastras in one shed or house, arranged in two rows, along the sides of the building.

The ground ore is now removed to provisional tanks formed of masonry or rough boards propped up by large stones, the joints being luted with clay and horse-dung, in which the ore undergoes spontaneous evaporation from the heat of the sun. After drying in this manner it is removed to the court-yards or *patrios* of the smelting establishment, the floor of which is paved with stones, the joints of which are cemented to prevent the collection and loss of mercury in the crevices. Here the ore is placed in a *heap*, *pile*, or *torta*, of dimensions varying with the amount of the materials, a pile containing 50 tons measuring about 50 feet in diameter, and is made from 10 inches to 12 inches high. Upon the top of this heap is sprinkled from 1 per cent. to 5 per cent. of common salt (NaCl), which is allowed to melt gradually, taking care not to use too much water in the operation, and to mix the materials so as to render the heap as homogeneous as possible, the pile being trodden by horses, or mules, moving over it for several hours. The horses begin at the circumference and passing round, gradually work towards the centre, while a number of men shovel in and turn over the ore at the circumference, this trampling and mixing of the materials being known as a *repaso*. The mixture is now allowed to remain at rest for twenty-four hours or longer, when the process of *incorporation* or mixing with "*magistral*" ensues, the *magistral* being a substance produced by the roasting of yellow copper ore, or sulphide of copper and iron, at a carefully regulated and low temperature, so as to produce

as much cupric sulphate as possible. From 1 per cent. to 2 per cent. of this substance is now mixed with the ore, the incorporation being effected as before by the trampling of horses, while the mass becomes warm and spongy from the double decomposition between the cupric sulphate and sodic chloride in the mass. When the mixture is completed, mercury is added by squirting it from a leather or canvas bag over the surface of the heap, not more than two-thirds of the total amount of mercury to be added being made at the first addition, and this is mixed as before by a *repaso* or trampling of horses, mules, or men, or, latterly, a machine has been introduced for effecting this mixture.

Samples of the mass are taken at intervals for assay by washing in a vanning bowl; and when the assays show that the process is progressing too slowly, then the addition of a further quantity of magistral is made; or if it be too active from the presence of too much magistral, as indicated by the very grey and subdivided state of the mercury, it is retarded by the introduction of lime, chalk, or ashes; while when the assay indicates that the whole of the mercury has been taken up, which happens after a period depending upon the nature of the ore, the purity of the ingredients added, the temperature, etc., a second addition of mercury is made to the extent of about three-eighths of the quantity originally added, the mixture being effected by the trampling of horses, and specimens taken for assay as before; while fresh additions of mercury in continually smaller amounts are made, until the assays show that the whole of the silver has been amalgamated with the mercury, which usually occurs on from the 25th to the 50th day, according to the above conditions of ore, temperature, elevation of place above the sea-level, etc. In this manner an amount of mercury, from four to six times the amount of the silver to be extracted, is added to the mass, a somewhat larger proportion being added than is necessary to complete the reaction in order to obtain a fluid amalgam, and prevent loss from the escape of a fine dust of an amalgam of silver and mercury, which exists in the earlier stages of the amalgamation, when there is an insufficiency of mercury present in the pile.

The amalgamation being completed, the heap or torta, as

it is called, of ore or mud is transferred to large deep circular stone vats, where it is mixed with a further quantity of mercury, and a considerable proportion of water, the latter also running through the tank the whole time; while the mixture is agitated by a revolving paddle turned by mules. By this treatment the heavy amalgam, together with other heavy metalliferous matters, collect in the bottoms of the vats, while the lighter earthy impurities are held longer in suspension by the water, and are carried off by it.

The fluid amalgam thus obtained from the vats is squeezed through strong canvas bags, by which the excess of mercury necessary to retain the liquidity of the amalgam is forced out, and is returned to the next amalgamation; while there remains behind a solid or pasty argentiferous amalgam containing about one-sixth of its weight of silver, this is compressed into triangular segments, which are transferred to the *burning-house* for the separation of the mercury by the application of heat to the amalgam.

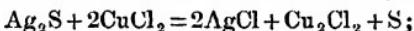
The *burning-house* consists of an iron stand or grate, with a hole through its centre, and upon which are placed the segments of the amalgam, six of the latter when placed together forming a circular disc or annulus, with a hole through the centre; the iron stand communicates by a pipe from its centre with a vat or reservoir of water placed beneath for condensing the mercury, as it distils downwards on the application of heat. The pile of amalgam, placed upon one stand, and weighing from 600 lbs. to 2000 lbs., is covered with an iron or copper bell (*capellina*), measuring about 3 ft. 6 in. in height, 1 ft. 6 in. in diameter, and 2 in. in thickness, which is suspended by a chain from above, the lower edges of the bell being luted down to prevent the escape of mercury except into the condensing vat beneath. Around the bell a loose open wall or brick cylinder is built, leaving an open annulus around the bell, in which a charcoal fire is made and maintained, when in about 8 hours (though this sometimes extends to 16 or 20 hours), the whole of the mercury is volatilised and condensed in the tank beneath, leaving a mass of spongy silver upon the stand, which only requires to be fused upon a cupel to fit it for commerce.

The *reactions* involved in the Mexican amalgamation

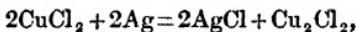
process are not well understood; but the first object in the process is to convert the argentic sulphide (Ag_2S) into chloride, effected by exposing a mixture of argentic sulphide and common salt to the action of air and moisture, as in the first stage of the process, when an amount of argentic chloride is produced; and, again, on the addition of *magistral*, the active constituents of which are cuprous and ferrous sulphates, double decomposition ensues, with a rise of temperature and the production of cupric chloride (CuCl_2) and sodic sulphate, thus—



while the cupric chloride so produced, in the presence of cuprous sulphate and sodic chloride, converts argentic sulphide into chloride, probably in the following manner:—



while the resulting cuprous chloride (Cu_2Cl_2), together with a further proportion probably formed by the reaction of silver upon cupric chloride, thus—



in the presence of air and sodic chloride, reacts upon a further portion of argentic sulphide, with the production of argentic chloride and a greenish-white residue of oxychloride of copper,



The argentic chloride formed, as the result of these reactions between argentic sulphide, sodic chloride, and cupric chloride from the *magistral*, is then acted upon by the mercury added for the amalgamation, with the production of mercurous chloride (Hg_2Cl_2) and metallic silver (p. 241), which amalgamates with the excess of mercury present.

The loss of mercury in this process, or, as it is called, "*consumed mercury*," amounts to from one-fourth to twice the weight of the silver extracted, the loss arising from the reduction of the argentic chloride by mercury as above noted, when the mercurous chloride (calomel) so produced is entirely lost; a further portion assumes a very fine state of division in the ore, known as *flouring*, and is mechanically lost; while if a portion of the copper should still exist in the state of cupric chloride (CuCl_2) from the addition of too much *magistral*,

then, when the mercury is added, a further loss is introduced from the reduction of cupric to cuprous chloride (Cu_2Cl_2), with the consequent formation of mercurous chloride (Hg_2Cl_2); and thus for the economical success of the operation, the mass should be as free as possible from cupric chloride when the mercury is added. To avoid the loss from the production of calomel (Hg_2Cl_2), it has been proposed to use a copper amalgam instead of pure mercury, by which it was thought to reduce the argentic chloride by the copper, while the silver so reduced should at once be taken up by the mercury, but the results attending its use have not been satisfactory. In lieu of the magistral, roasted iron pyrites is sometimes added, but a material containing copper is preferred; while instead of roasting copper pyrites for the production of magistral, it has been proposed to utilise the cupric sulphate produced in the "parting house," described when treating of gold.

The loss of silver in the Mexican method of amalgamation is also considerable, amounting to from $\frac{1}{8}$ th to $\frac{1}{4}$ th of the total amount in the ore.

117. **The Freiberg or European Method of Amalgamation.**—The method formerly pursued at Freiberg, and still carried on in Hungary, Spain, and some parts of Mexico, Nevada, California, etc., differs from the last described, inasmuch as the *chlorination* of the ore is effected in the dry way by roasting the ore in a reverberatory furnace with common salt; and the decomposition of the argentic chloride so produced is effected by means of *iron*, while the *amalgamation* is conducted in revolving *casks*, instead of in heaps exposed to the atmosphere as in the Mexican process. This method of amalgamation involves a *larger expenditure of fuel and water power* than the Mexican plan, and both these agents are abundant in the localities where it is employed, but it requires the expenditure of *much less labour* with a *decreased consumption of mercury*.

The ores treated at Freiberg by this process are of several classes, in which the silver amounts to from 15 to 200 oz. per ton of the ore. They occur in combination with sulphur, and are accompanied by *iron pyrites*, with the sulphides of copper, lead, and bismuth, and occasionally also antimony and arsenic; but the presence of *iron pyrites* is essential to the success of

the process, and requires to be added if not present in sufficient quantity; while the ores should not contain more than from 3 per cent. to 5 per cent. of lead (galena), or about 1 per cent. of copper, the ores containing these metals in larger proportions being much more conveniently and economically treated by dry smelting as described under lead, etc. The process is not therefore applicable to the treatment of argentiferous galenas, blendes, or copper pyrites, or to ores containing more than 1 per cent. of arsenic.

The treatment of ores of silver by the Freiberg process involves four operations, viz. :—

1°. *Roasting* with common salt in the presence of a sufficient quantity, about 25 per cent. of iron pyrites.

2°. *Grinding* of the roasted product.

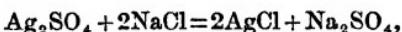
3°. *Decomposition* by wrought iron, and *amalgamation* in revolving barrels or casks.

4°. *Distillation* of the silver amalgam.

The ores having been reduced to powder and mixed together, so as to contain an average of from 30 to 40 oz. of silver per ton when treating poor ores, or from 90 to 130 oz. when treating richer ores, with sufficient pyrites (as determined by a previous assay) to carry on the necessary reactions, are mixed with from 5 to 10 or 15 per cent. of common salt (NaCl), and transferred in charges of about $4\frac{1}{2}$ cwt. to flat bedded *reverberatory calciners*; that known as the *Hungarian* furnace having a bed formed in two steps, the higher one being nearest the stack, while near the stack and over the furnace are chambers (soot chambers or condensers), through which the gaseous current passes before reaching the stack, and in which metallic particles, etc., carried over with the gases, are deposited and collected.

The *roasting* is conducted in two stages, in which the utmost care is required to properly regulate the temperature. The ore mixture is charged through a funnel-like tube on to the upper step or bed of the furnace, where it is roasted in an oxidizing current at a temperature gradually raised to redness, by which means water vapour and sulphurous anhydride are evolved, along with fumes of the oxides of arsenic and antimony, if these metals be present in the ore; while the iron pyrites is converted largely into ferrous sulphate. On the com-

pletion of this stage the temperature is raised, and the last named salt is decomposed, as described in Vol. I., p. 43, with the evolution of sulphurous anhydride (SO_2) and sulphuric anhydride (SO_3), the latter by combination with the silver compounds producing argentic sulphate, which resists a much stronger heat than ferrous sulphate, without undergoing decomposition; while in the next stage, conducted on the lower bed of the furnace, the argentic sulphate thus produced, and the common salt (NaCl) added with the charge, react upon each other with the production of argentic chloride and sodic sulphate,



an intimate mixture of the materials being maintained throughout, by continued rabbling or stirring of the mass through a side door of the furnace provided for the purpose.

The ore loses about 10 per cent. of its weight during the roasting process, and the product, which has a brown colour from the presence of ferric oxide, etc., now contains the silver almost wholly in the state of argentic chloride, with a little metallic silver; and, besides the earthy matters of the ore, it contains in addition cupric and ferric chlorides and sulphates, with common salt and sodic sulphate. It is now ground exceedingly fine, any clots that may have been formed during the roasting being ground and put aside for recalcination with common salt. The ore, after grinding, passes through a fine sieve or bolting-cloth, and is then conveyed to the amalgamating barrels.

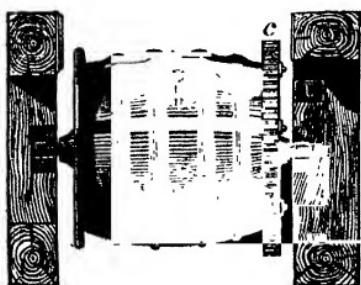


Fig. 51.—CASK USED IN THE EUROPEAN METHOD OF AMALGAMATION.

The reduction of the argentic chloride by scrap iron, and the amalgamation of the silver with mercury, is effected in strong rotating wooden casks *a*, fig. 51, measuring about 3 ft. in length, and 2 ft. 9 in. in maximum diameter, which are fixed upon horizontal axes *b*, *b*, and rotated by the spur-wheel *c*, fixed at one extremity of the casks, and which gears with

a driving wheel *d*, fig. 52, keyed to a shaft driven by water power, while a suitable arrangement permits of the barrels being readily thrown in and out of gear so as to stop or start the rotation as required. The casks are well hooped and strengthened by iron bands, while the bung or stopper *e*, for closing the aperture employed for the introduction of the charge, is formed in two parts, viz., an outer annulus and a central plug, both of which are withdrawn for the introduction of the ore and water into the casks, while the central part only is withdrawn for the introduction of the mercury, and withdrawal of the amalgain after the manner to be described. About 20 of these barrels are arranged in one machine, while over each barrel, and resting upon the upper floor of the amalgamating houses, is placed a hopper or chest *f*, fig. 52, containing the proper amount of ore required for one charge of the barrel. The chest *f* communicates with the barrel or cask by the funnel-shaped tube *g*, terminated by the flexible hose *h*, which is inserted into the aperture in the cask, and so the powdered ore is introduced; while a tank *k* holds the amount of water required for each charge of the barrel, which it empties by a pipe into the cask, and the mercury contained in a reservoir is connected with the apparatus by the trough *b*.

In charging the casks, they are placed with the aperture *e* in a vertical position, and about 35 gallons of water succeeded by about 10 cwt. of the roasted ore, and finally from 80 to 100 or 110 lbs. of *wrought iron*, in the form of small bars of about $1\frac{1}{2}$ in. square and $\frac{7}{8}$ ths in. thick, are introduced. The stopper or bung is then screwed in and secured as shown, after which the barrels are set in rotation, at the rate of from 14 to 16 revolutions per minute, and the rotation continued

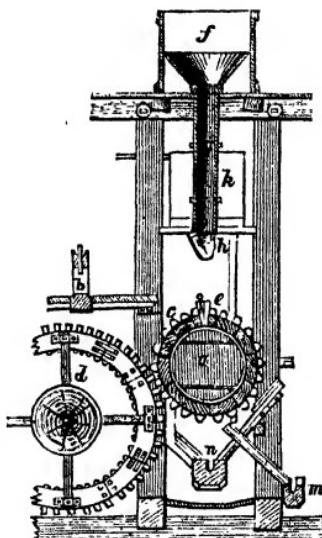


Fig. 52.—FREIBERG BARREL
AMALGAMATION APPARATUS.

for a period of from $1\frac{1}{2}$ to 2 hours, during which process the soluble salts formed during the roasting operation are dissolved out by the water.

After revolving for some time the temperature gradually rises, and a double decomposition ensues between the *argentite chloride* and the *wrought iron*, by which ferrous chloride is formed, and metallic silver liberated; and at the same time ferric and cupric chlorides, present in the mother liquor, are reduced by the iron to the state of ferrous and cuprous chlorides respectively. The contents of the casks are now in a state of perfect incorporation, and should have the consistency necessary to allow of its thorough mixture and the ready amalgamation of the silver with the mercury without being too fluid, otherwise the mercury falls directly to the bottom of the barrel without becoming thoroughly incorporated with the charge, which should now occupy about two-thirds of the capacity of the barrel. The rotation is now stopped, and the central plug of the stopper *e* withdrawn, when about 5 cwt. of mercury is run from the trough *b* into each barrel; and after reinsertion of the stopper, the whole is again set in motion at the rate of from 16 to 20 revolutions per minute, the speed of rotation being important, for if too slow the materials adhere to the sides of the cask so firmly that no subsequent movement suffices to detach it, while if too quick, the action proceeds with increased rapidity, and the temperature rises too high, a temperature of about 32°C . (90°F .) appearing to be best suited to the process.

When the amalgamation is judged to be complete, the rotation is stopped. The casks are then almost filled up with water and the motion resumed, but more slowly, for about two hours, so as to better collect into one mass the dispersed globules of amalgam, when the revolution again ceases and the casks are turned with the bung or stopper *e* downwards, so that on withdrawing the central portion of the bung and inserting into the aperture a leather tube fitted with a stop-cock and mouthpiece, the amalgam can be drawn off into the trough *m*, which conveys it to a tank where it is agitated or stirred continually by a rotating vertical spindle carrying vanes or arms; and by this treatment the heavy amalgam is separated as thoroughly as possible

from the uncombined mercury and other residues accompanying it.

The residue left in the casks, after drawing off the amalgam, often retains from '008 to '016 per cent. of silver; it is emptied into the middle trough or channel *n*, and passes in its course through an iron grating or sieve to separate the pieces of iron from the argentiferous mud, etc.; when the latter, if it holds upwards of 4 oz. of silver per ton, is, after well washing to separate the earthy matters as thoroughly as possible, then dried, re-roasted, and again amalgamated. The mother liquor obtained from the casks, as also from the washing of the mud, contains sodic chloride and sulphate, ferrous and manganous sulphates, with small quantities of phosphates, etc.

The amalgam obtained in the above manner is introduced into strong canvas bags as in the Mexican process, when, on the application of a gentle pressure, a fluid amalgam of mercury and silver containing from '003 to '005 per cent. of the latter exudes through the material of the bag, and is again used in a subsequent amalgamation; while a pasty or semi-solid amalgam consisting of about 84 per cent. of mercury, with from 10 to 12 per cent. of silver, about 5 per cent. of copper, together with traces of tin and lead remains, and is subjected to the fourth or distilling operation.

The decompositions carried on in the amalgamating barrels are not confined to the reaction between argentic chloride and metallic iron, but other metallic chlorides produced during the roasting process are also reduced by the iron, and pass in larger or smaller proportion into the resulting amalgam, while any metallic copper thus separated immediately reacts upon argentic chloride, with the formation of cuprous chloride, and the precipitation of metallic silver; and it is desirable that these reactions, especially the reduction of argentic chloride, ferric chloride, and cupric chloride, to metallic silver with ferrous and cuprous chlorides respectively, be as complete as possible before the addition of the mercury, otherwise a loss of mercury occurs from the production of calomel in the same manner as described in the Mexican plan of amalgamation, p. 245.

The distillation of the amalgam was originally conducted

per descensum in an apparatus (fig. 53) consisting of small brick furnaces, several of which are built together. In the

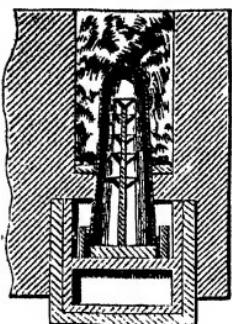


Fig. 53.—FURNACE FOR THE DISTILLATION OF AMALGAM.

or 8 hours; while care is taken that the temperature be never allowed to become sufficiently high as to volatilise any of the silver along with the mercury; yet if the temperature be too low, the silver is only imperfectly freed from mercury, and a loss of the latter is entailed. The mercury distilled from the amalgam in this manner is condensed in the water in which the apparatus stands, cooling of the latter being further promoted by the circulation of cold water around it. The spongy metallic mass left in the dishes after this treatment is often very impure, containing but about 75 per cent. of silver, the residue consisting largely of copper along with lead, bismuth, zinc, and antimony in variable proportions; and to free it from these impurities it is melted either in crucibles or on the bed of a reverberatory furnace, and stirred or rabbled with an iron rod, by which means the oxides of arsenic, bismuth, zinc, and antimony escape largely as white fumes, while a proportion of the oxides of copper and lead collect as a scum on the metal, and are removed before casting the metal into ingots; the silver now contains about 98 per cent. of the pure metal, but for the complete separation of the impurities, especially of copper, it is alloyed with a further quantity of lead, and subjected to the operation of cupellation.

To overcome the difficulty arising from cracking of the

ells and the incomplete separation of the mercury in the above distillatory apparatus, *iron retorts*, fig. 54, have been substituted. These are formed of an iron body *a*, of the shape of a crucible of about 11 inches in diameter and 20 inches in height, to which is fitted a hood or neck *b*, and a condensing tube *c*, both of iron, the latter passing through a cistern (*d*) of water for keeping it cool; but it is advisable to supersede the latter by making the tube (*c*) of sufficient length and diameter to condense the mercury without recourse to the cooling by water. The crucible of the retort is heated by a charcoal fire, when the mercury distils off and collects as in an ordinary distillation in a receptacle *e*, at the end of the condensing tube. The crucible is lined internally with a coating of lime, as is also an iron plate placed within the retort, and to which the spongy silver adheres when the distillation is completed. For this apparatus the charge is about 4 cwts. of the amalgam, from which the mercury is distilled in about 10 hours.

Another form of the cast-iron retort consists of a cylinder, the front end of which is fitted with a movable cover which is affixed when the charge of amalgam has been introduced, while from the highest point of the rear or closed end of the retort the mercurial vapours are conveyed downwards by a pipe, which is cooled by the circulation of water around it.

The silver obtained as the result of these distillations is still alloyed with small proportions of various other metals, and is hence subjected to a preliminary refining by melting the metal in a crucible, with its surface covered with charcoal, the latter, along with dross, etc., being subsequently removed from the surface by a perforated ladle, and the operation repeated until the surface of the melted metal becomes perfectly clear, upon which it is cast into ingots, and is then ready for the mint.

In the European method of amalgamation the loss of mercury amounts to from 20 per cent. to 25 per cent. of the

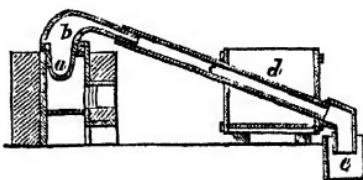


Fig. 54. — RETORT FOR THE DISTILLATION OF AMALGAM.

amount of the fine silver produced, or about .05 per cent. of the weight of the ore amalgamated, thus effecting a considerable saving in mercury over the Mexican plan of amalgamation; while the loss of silver in the Freiberg (European) process is only from 5 per cent. to 9 per cent. of that contained in the ore, as against from 12 per cent. to 25 per cent. lost in the Mexican method.

118. Amalgamation of Copper Regulus.—If copper regulus, i.e., the product produced in copper smelting corresponding to the Welsh *fine metal*, or the *black-copper* obtained in the Mansfeld and other continental copper smelting works, contain upwards of .025 per cent. of silver, it may be extracted by the European method of amalgamation; for which purpose the regulus is heated to redness in a reverberatory furnace having a bed of cast-iron, and broken when hot by stamps, reheating and stamping again being repeated until the material is sufficiently fine; after which it is ground between stones to a fine powder, and then roasted in charges of about 4 cwt. each on the bed of a reverberatory furnace, the mass being continually rabbled during the roasting. When this roasting is completed the mass is raked from the furnace, allowed to cool, and mixed with from 7 to 10 per cent. of common salt, and a like amount of calcic carbonate, which mixture is made into a paste with water, then dried, and finally reduced to a fine powder, when it is roasted a second time at a much higher temperature than before. The argentic chloride so produced is usually decomposed by copper or iron in casks similar to those already described for the Freiberg process, and in which the amalgamation is effected, the treatment and amalgamation of the roasted regulus being conducted after much the same manner as that already described; while the silver is refined as before by fusion in black lead crucibles. But the silver from highly argentiferous copper matts or regulii is always extracted by treatment according to the wet methods of Augustin or Zier vogel.

119. Amalgamation of Argentiferous Speise.—The compound of nickel, cobalt, iron, arsenic, and antimony, with bismuth and other metals, frequently containing also sulphur, and which constitutes the *speise* produced in the Saxon works

during the manufacture of smelts, often contains from 10 grs. to 100 oz. of silver per ton, and this is usually extracted by the *amalgamation method*, for which purpose the speise, after being ground to powder, undergoes a preliminary treatment, by which a portion of the arsenic and other volatile elements are volatilised in the form of arsenious anhydride, etc. The residue from this roasting is sifted to separate clotted and un-oxidized portions, and after again grinding to a fine powder is mixed with about 8 per cent. of *common salt* and 2 per cent. of *ferrous sulphate*, and then roasted as in the Freiberg process, when the resulting product, containing the silver in the form of argentic chloride, is treated in *barrels* or *casks* along with *wrought iron*, and subsequently *amalgamated* after the European method of amalgamation. The loss of silver in this treatment amounts to about 15 per cent. of the amount originally contained in the speise, while the waste of mercury is only about 15 oz. per ton of material operated upon.

In Upper Hungary the treatment is somewhat different. The *speise*, containing about 28 per cent. of silver, is mixed with 2 per cent. of limestone and roasted for about 5 hours on each of the hearths of the Hungarian furnace described on p. 247, after which the roasted ore is sifted, mixed with 1 per cent. of lime and 7 per cent. of common salt, and again roasted during about 6 hours; when after cooling, grinding, and mixing with a further proportion of lime, it is made into a paste with a solution of common salt, then introduced into a cask along with metallic copper and rotated at the rate of about twenty-five revolutions per minute during five hours, on the completion of which an addition of mercury to the extent of about one-third the weight of the ore is made, and the rotation continued at the rate of some eighteen revolutions per minute during a further period of fifteen hours. The amalgam thus produced affords, after squeezing out the excess of mercury, a granular mass containing about 18 per cent. of silver.

120. Method of Amalgamation in Kettles.—In this method, known also as the *hot amalgamation*, the ores are treated in kettles with copper bottoms, whereby the silver is precipitated from its chloride, bromide, or iodide, and subsequently amalgamated by the addition of mercury; the

method is, however, only applied to the treatment of certain comparatively rich ores containing chloride, bromide, and iodide of silver, accompanied also by native silver, and is chiefly in use in South America.

The ores are crushed and ground to a fine powder, concentrated if necessary by careful washing, and then mixed with a large proportion of water, thus forming a thin mud which is introduced into *kettles* or boilers provided with copper bottoms.* The contents of the kettle are now heated to boiling by a wood fire maintained in a fireplace beneath the kettle, when from 10 to 15 per cent. of common salt is thoroughly mixed with the charge, after which a quantity of mercury is added and incorporated with the mixture by continuous stirring, the temperature of the contents of the kettle being kept up throughout the process, while samples of the amalgam are removed at intervals, and from their examination the attendant determines when the amalgamation is completed, as also whether any and how much more mercury it is necessary to add to complete the operation, the whole treatment usually lasting from five to six hours. The amalgam thus obtained is treated according to the methods already described by distillation in iron retorts, the silver produced requiring, as before, to be fused and refined before casting into ingots for commerce; while the earthy residues left after the separation of the amalgam frequently retain sufficient silver to render them worth treatment by the method of *amalgamation in heaps*.

The consumption of mercury in this process is usually somewhat less than the weight of the silver extracted, in which respect it thus stands intermediate between the Mexican and European plans of amalgamation.

WET METHODS FOR THE EXTRACTION OF SILVER.

For the treatment of argentiferous metallurgic products, as copper or other regulus, matts, speise, etc., and of such ores as are suited to the amalgamation processes, *wet methods* of extraction have largely superseded the older methods of

* Lamborn, *Metallurgy of Silver*.

liquation and amalgamation; the wet processes being alike *more simple, less costly, and more rapid* than the processes of liquation and amalgamation, besides exceeding these operations in the *completeness* of the extraction of the silver, and in being much *more healthy* for the labourers employed upon them, while avoiding the large loss arising from the consumption of mercury in the amalgamation processes, and not requiring the amount of fuel necessary for the methods of liquation or fusion with lead. The ores for treatment by the wet methods should not, however, be too rich in silver, and at the same time they are required to contain but small proportions of lead, zinc, antimony, or arsenic, especially if for treatment by the process of Ziervogel; while the presence of either cuprous sulphide or iron pyrites is necessary to produce the reactions of the roasting stage of these processes.

The more important *wet methods* for the extraction of silver from ores, regulus, etc., are—

I. The *method of Augustin*, in which argentic chloride, formed by roasting the ore or regulus with common salt, is extracted by a *solution of common salt*, and the silver precipitated therefrom by metallic copper.

II. *Ziervogel's process*, in which, by a careful roasting of the ore or regulus, the iron, copper, etc., are converted into oxides, while the silver is converted into the soluble *sulphate*, which is then extracted by *warm water*, and the silver separated by precipitation.

III. *Von Patera's method*, in which the silver is converted into chloride after the manner employed by Augustin, and the argentic chloride then dissolved out by a cold solution of *sodic-hyposulphite* ($\text{Na}_2\text{S}_2\text{O}_3$); from which solution the silver is again precipitated as *sulphide* by the addition of *sodic-sulphide*, and the silver extracted from this sulphide by heating in a retort or muffle.

121. Augustin's Method of Extracting Silver.—This method, employed in Saxony, Hungary, Swansea, etc., for the extraction of silver from *copper regulus*, *argentiferous copper ores*, *argentiferous pyrites*, etc., depends for its success upon the production of *argentic chloride* by the careful roasting of the cuprous product with *common salt*, after the manner and according to the reactions described under the Freiberg

process of amalgamation, page 247, together with the solubility of the argentic chloride so produced in a hot solution of common salt; from which solution the silver can be precipitated by metallic copper. This process, accordingly, differs from the Freiberg or European method of amalgamation only in the method of extracting the silver from the argentic chloride produced in the roasting operation; Augustin substituting a solution of *common salt* for the mercury employed in the amalgamation process.

The argentiferous copper ores are smelted, as in the ordinary course of copper smelting, for the production of a regulus or matt containing from 60 to 70 per cent of copper, with from .4 to .5 per cent. of silver, such a regulus containing, as usual, iron with small quantities of antimony, arsenic, etc.; but it is desirable that the *matt* to be treated by this process should be as free as possible from these latter elements. The regulus is broken up and stamped while in a moist state, or is ground between rollers to a very fine powder, which is then passed through a sieve of some 1500 or 2000 meshes to the square inch. The finely-powdered regulus is now transferred, in charges of from 4 to 12 cwts., to the hearth of a reverberatory furnace, where it is roasted during five hours; in the first stage of which, lasting from two to two and a half hours, the temperature is carefully regulated so as not to rise too high, while the mass is kept continually stirred, and during this period sulphurous anhydride is copiously evolved; while in the second stage, lasting from two to three hours, the heat, gradually rising in the previous stage, now becomes considerable, and is attended with the evolution of white fumes of sulphuric anhydride (SO_3), produced chiefly by the decomposition of the ferrous and cuprous sulphates formed during the oxidation in the first stage. The roasting again requires considerable care that the temperature be raised sufficiently high to decompose the whole of these sulphates (especially the ferrous salt), converting them into oxides whilst leaving the argentic sulphate undecomposed. The ore is thus roasted quite *sweet*, and a portion taken out for trial from near the fire-bridge should, on treatment with water and common salt, leave on filtering a solution having a faint blue tint; but if any green colour is discernible, it

indicates the presence of ferrous sulphate, and the roasting is not completed. The roasted mass, which has now a brown, earthy appearance, is raked from the furnace, allowed to cool, and then ground to a fine powder under rolls; after which it is again introduced, but in smaller charges, into the calciner or reverberatory furnace, where it is roasted for a short time, and then mixed with about 5 per cent. of common salt, and the roasting continued, with frequent stirring, during a further period of about three hours. By this means the silver is converted into chloride, according to the reactions already explained, page 248, when the mass is withdrawn from the furnace to be lixiviated.

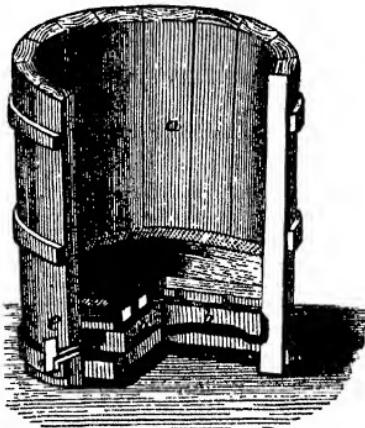
The *lixiviation* of the *roasted* and *chlorinised* ore is conducted in tubs or barrels

a, fig. 55, possessing false bottoms, formed by placing upon the true bottom of the tub a wooden cross *b*, on which is placed a perforated disc or board, which is again covered with a layer of twigs or straw, over which is again stretched a linen cloth, the whole forming a kind of filter; while communicating with the space between the true and false bottoms

is a cock *e* for drawing off

Fig. 55.—TUB USED FOR LIXIVIATION
IN AUGUSTIN'S PROCESS.

the solution. A series of these vats are arranged in tiers, while into each vat or tub of the top tier is introduced about 8 cwt. of the materials still heated from the roasting process, and on to this is directed from the tank *a*, fig. 56, along the trough *b*, a hot and tolerably strong solution of *common salt*, which is distributed over the surface of the charge by the small pipes *c*, *c*, and through a perforated top, thus rendering the solvent action as uniform as possible, by preventing the formation of channels within the mass. The materials for lixiviation being hot, steam is generated in the tubs, and the finely-divided argentic chloride



is dissolved by the solution of brine, which solution filters through the false bottom of the vat, and is then drawn off through the stop-cock into a *settling vat* placed above the uppermost tub *d* shown in the figure, and where any particles mechanically held in suspension are allowed to subside; after which the liquid is drawn off into the first of the series of *precipitating vats* placed on the tier immediately below the last. The precipitating vats are similar in construction to the first described, except that there is placed upon the false bottom a layer, some 6 or 7 inches in depth, of *cement copper*, which decomposes the argentic chloride, with the production of cuprous chloride and the precipitation of metallic silver;

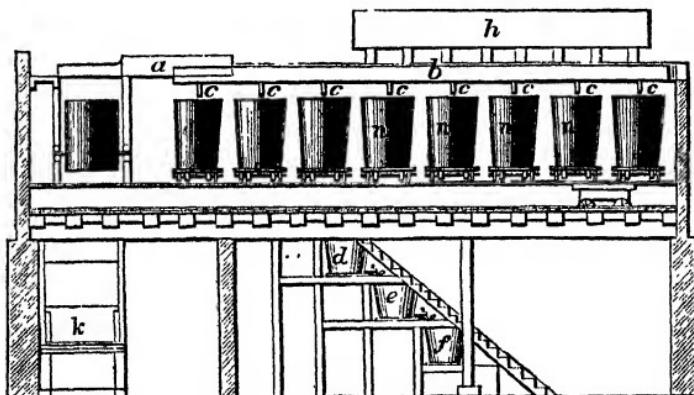


Fig. 56.—ARRANGEMENT OF THE VATS FOR THE AUGUSTIN OR ZIERVOGEL PROCESS.

the precipitation of the whole of the silver being ensured by withdrawing the liquor from the last tier to a second tier (*d*) of precipitating vats placed immediately below; and after remaining here some time, the mother liquor is drawn off into the last tiers of vats *e*, *f*, containing metallic iron, and in which the cuprous chloride formed in the previous reactions is decomposed, with the deposition of cement copper, and the production of ferrous chloride.

The solution of brine is passed over the charge of roasted materials in the first or lixiviation tub, so long as it dissolves out any argentic chloride, as determined by the non-

deposition of a silver coating upon a plate of copper introduced into the stream running from the stop-cock. And the cement copper deposited in the last vats is returned at intervals to the precipitating vats, whereby the same copper is made to do duty for two or three times; while the brine escaping from the last tubs is exposed to the atmosphere for some time, by which a great portion of the ferrous salts are oxidized, with the deposition of the iron in the form of a basic ferric salt, and the sodic sulphate produced during the roasting of the ore with common salt is either separated by evaporation or reconverted into common salt by the addition of cuprous chloride. The brine thus freed from iron and sodic sulphate is also returned to the reservoir *k* at the top, where it is heated and again used for a subsequent lixiviation.

The residues from the lixiviating vats consist largely of oxide of copper, and should not contain more than .035 per cent. of silver, when they are at once treated by fusion for the extraction of their copper; but if the residues are found to contain more than this limit of silver, they are re-roasted and again lixiviated before treating for the extraction of their copper. *k* is a drainer on to which the contents of the vessels (*n*) are emptied after the lixiviation is completed, so as to completely drain off any liquid portion.

Instead of drawing off the brine from the bottom of the vats in the manner described, an improved plan is adopted at Swansea, in which a tank is divided into four compartments, the brine flowing into the first compartment, which it fills, and then overflows the partition into the second compartment through which the liquid descends and passes by a communication in the bottom to the third compartment, through which it rises and overflows the partition into the fourth; scrap or cement copper being placed in the second and third compartments, after the manner described in the use of the vats.

The cement silver obtained from the precipitation vats is contaminated with particles of copper, from which it is freed by treatment with dilute hydrochloric acid. The silver is collected after every 8 or 10 days, dried, and transferred to the refinery before being forwarded to the mint.

The loss of silver in this method of treatment is from 8 to 12 per cent. of the assay produce of the regulus under treatment.

122. Ziervogel's Method of Extracting Silver. — This, which forms the most simple and economical plan for the extraction of silver, was introduced in 1857 at the Mansfeld works for extracting the silver from the argentiferous copper schist occurring in the district; and it has almost entirely superseded the method of Augustin previously in use, notwithstanding that it labours under the disadvantage of requiring that the ores be *pure*, and tolerably *uniform* both *in composition* and character; while the roasting, which constitutes the most important stage of the process, requires very considerable skill and care for its satisfactory performance, so that, as will be subsequently noted, a combination of the methods of Augustin and Ziervogel has been adopted at Swansea and other districts for the extraction of silver from argentiferous ores.

The Ziervogel process is not well adapted to the extraction of silver from ores containing *lead*, *zinc*, *arsenic*, or *antimony*, being inferior to the method of Augustin for the treatment of such ores, since in the former (Ziervogel) process insoluble arsenates and antimonates of silver are produced in the roasting and escape decomposition, causing thereby a loss of silver to the extent of about .0015 per cent. of the weight of regulus treated.

For treatment by the Ziervogel process, the copper schist is smelted as in the ordinary process of copper smelting, so as to give a *regulus* or *fine metal* containing from 60 to 70 per cent. of copper, with 6 or 7 per cent. of iron, and from 4 to 5 per cent. of silver, and which is then subjected to treatment by the Ziervogel process proper, involving, as noted above, two distinct operations: 1°, *roasting* of the finely-divided regulus until the iron, copper, etc., are converted into insoluble oxides, while the silver remains as a soluble *sulphate*; and 2°, *lixiviation* of the roasted mass with *warm water*, whereby the argentic sulphate is extracted, and subsequently treated with metallic copper for the precipitation of its silver.

The *regulus* is ground to a fine powder under granite rolls, and sifted through a sieve of from 1300 to 1500 meshes to the square inch, after which the charge of from 5 to 6 cwt. as employed at Mansfeld, or of about 12 cwt. adopted at Swansea, consisting of fresh regulus mixed with about one-sixth of its

weight of the imperfectly desilverised residues from a previous treatment, is transferred into a long reverberatory furnace, where it is roasted with the greatest care; or double-bedded furnaces have been used for this purpose, in which the upper bed formed a closed chamber or muffle heated from beneath by the flame passing over the lower bed, and from above by the flame deflected backwards and forwards in its course through a series of depositing flues or chambers built over it, and in which any particles mechanically carried over by the current of gases through the furnace are deposited, but the mechanical difficulties attending the use of this furnace have prevented its general adoption. The temperature of roasting is at first very moderate, during which the charge is frequently stirred and the heat gradually raised, while in about $1\frac{1}{2}$ hours the mass will have attained a cherry-red heat which is continued during about 10 hours, when the roasting approaches completion; or if the double-bedded furnace be employed, the first stage of about $5\frac{1}{2}$ hours is conducted upon the upper bed, when the mass is raked through an aperture on to the lower bed where the roasting is completed.

Trial samples are withdrawn from the furnace towards the end of the operation and dissolved in water, when, if the solution shows a faint blue colour without any tinge of green, the operation is considered complete.

The roasting, as in Augustin's process, is attended in the earlier stages with the evolution of sulphurous anhydride, succeeded towards the end, as the temperature increases, by white fumes of sulphuric anhydride (SO_3); while a loss of about 7 per cent. of the silver originally present occurs during the roasting process.

On the completion of this roasting, the charge which is of a dark colour, not clotted, but forming a pulverulent powder, is transferred for lixiviation to a series of tubs with false bottoms, and arranged in tiers (fig. 56), as described under the last article; while at Swansea, tanks, instead of tubs or barrels, are employed for this operation. The charge of from 4 to 5 cwt. of the roasted product, previously allowed to cool down, is introduced into each of the 10 tubs (A) of the uppermost tier, when *water*, a little sulphuric acid, and the mother liquor from a previous lixiviation, after the separation of its

copper and reheating by steam to about 87°C. (188°F.), are introduced on to the surface of the materials in the vats. These liquids, percolating through the mass of roasted powder, extract the soluble compounds, amongst which is argentic sulphate, about 2½ hours being thus required for the extraction of the soluble salts from each charge, while the presence of a little free sulphuric acid in the solution prevents the formation of basic salts. The solution, as it collects in the bottom of the vats, is drawn off into the first compartment (B) of the simple *settling* vats, from which it passes onwards into the second division C, separated from B by a partition

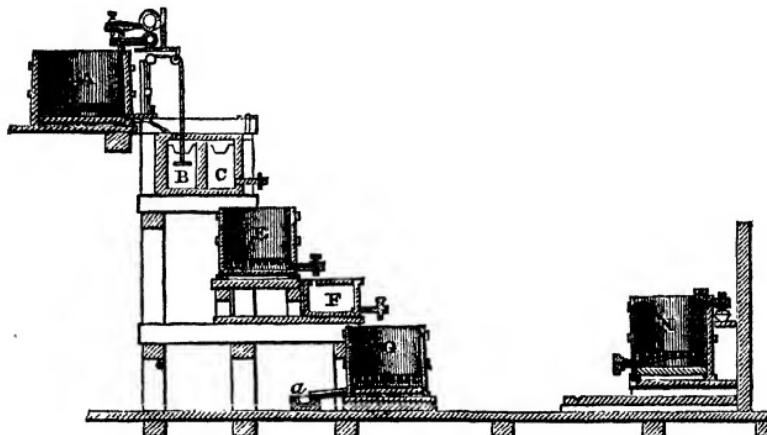


Fig. 57.—ARRANGEMENTS OF ZIERVOGEL'S APPARATUS.

which does not reach quite to the top, and over which the liquid flows from B to C; from C the solution is distributed into the ten precipitating vats E, each provided like A with false bottoms, upon which are placed some 10 lbs. of *granulated copper*, and about 2½ cwt. of *blister copper* in *bars*; and in these vessels the silver is precipitated as cement silver, while the liquid passes into the wooden trough F, on the bottom of which is a layer of small pieces of copper. The liquors are now introduced into the tubs G, also with false bottoms, and upon which is placed a little granulated, together with small bars of copper, after passing over which the desilverised fluids are conveyed by a gutter *a* to a pan where they are reheated to 87°C., again raised to the top of the apparatus,

and used again in the lixiviation of a further charge introduced into the lixiviating vats. The vat N is employed for washing and treating the residues from G.

The silver almost wholly collects in the first of the precipitating vats, only a small proportion passing on to the lowest tier, and the deposited silver is collected therefrom at intervals of about 24 hours, when it usually contains about 20 per cent. of impurities, consisting of calcic sulphate, cupric sulphate, metallic copper, etc., of which the two former are extracted by repeated washing of the deposit, while the latter is largely removed by acting upon the metal with dilute hydrochloric acid; when, after refining by fusion, the silver is ready for forwarding to the mint.

The loss of silver in the Ziervogel process amounts to from 6 to 7 oz. per ton of the regulus treated; but the refined copper produced at Mansfeld from the residues, after treatment by amalgamation and Augustin's process, yields from .0388 to .0631 per cent. of silver,* whilst in 1861, with the introduction of the Ziervogel process, the refined copper contained only .0215 per cent. of silver.

123. Extraction of Silver by the Combined Methods of Augustin and Ziervogel.—At Swansea, a combination of the methods of Ziervogel and Augustin is adopted in the treatment of certain classes of argentiferous copper ores, according to which plan the ores are first roasted as in the Ziervogel process for the production of argentic sulphate, which is extracted as thoroughly as possible by means of hot water, when there is usually left in the residues about 20 oz. of silver in the ton, for the extraction of which the residues are dried and carefully re-roasted with an admixture of about 3 per cent. of common salt, when the argentic chloride so produced is extracted by a solution of brine (NaCl) according to Augustin's method, and by this means a further proportion of from 12 to 14 oz. of silver per ton of material is extracted, leaving from 6 to 7 oz. per ton which is lost.

124. Loss of Silver in its Extraction.—The loss of silver in treating the *matts* produced in the smelting of the argentiferous copper schists of Mansfeld, amounts to nearly 10 per cent. of the silver present, if treated by the *amalgamation*

* Phillips' *Metallurgy of Gold and Silver*.

process; by *Augustin's* process to about 8 per cent.; while in *Ziervogel's* process the loss forms less than 1 per cent. of the silver originally present in the regulus.

125. Von Patera's Method of Extracting Silver.—This method, applied to the rich ores of the Joachimsthal district of Bohemia, is based upon the ready solubility of argentic chloride in a solution of sodic hyposulphite ($\text{Na}_2\text{S}_2\text{O}_3$), a quality first observed and communicated in a paper by Dr. Percy in 1848. The extraction of silver by this method, like the wet methods already described, involves *four* distinct operations, viz.:—1°. *Roasting* of the ore in a particular manner, for the conversion of the silver wholly into argentic chloride. 2°. *Lixiviation* of the roasted mass in a solution of *sodic hyposulphite*. 3°. *Precipitation* of the metal as *argentic sulphide* by the cautious addition of *sodium sulphide*. 4°. *Reduction and refining* of the argentic sulphide produced in the last operation.

The ores worked by this process are remarkably rich, containing an average of from 2 per cent. to 3 per cent. of silver, while some varieties yield as much as 12 per cent. or 14 per cent. of the precious metal, the associates consisting of copper, iron, nickel, cobalt, lead, bismuth, sulphur, oxygen, arsenic, and antimony, the process being especially applicable to the treatment of rich ores containing nickel and cobalt, which it is desired to separate and utilise.

The ore is first picked for the separation of the poorer portions, then reduced to powder and roasted in two stages. The first stage is conducted upon charges of about 4 cwt. placed upon the bed of a reverberatory furnace, of "somewhat peculiar construction, and over which a current of steam passes during the roasting. Instead of the long hearth usually adopted in reverberatory furnaces, the furnace here employed has a hearth measuring about 6 ft. from the fire-bridge to the flue end, while from back to front it measures from 9 to 10 ft.; the *fireplace* also is only some 6 or 9 inches wide, but extends from back to front for nearly the full depth of the hearth, by which means a broad sheet of flame is maintained on the hearth, producing a very uniform temperature over every portion of its surface. The *fire-bridge*, again, is tubular and narrow, and so absorbs little heat; while a number of open-

ings are made from it on to the hearth, so that steam supplied to the bridge by a special boiler is distributed over the roasting mass. The bridge is frequently constructed of an iron tube coated with clay, and perforated with a number of openings on the side towards the hearth.

After the introduction of the charge into the furnace, the heat is gradually raised until the mass attains a red heat, when the steam is admitted to the hearth, and the temperature maintained as high as possible without clotting the ore. This stage lasts about 4 hours, when the ore is withdrawn, and after cooling is ground to powder and mixed with from 6 per cent. to 12 per cent. of sodic chloride, with 2 per cent. to 3 per cent. of ferrous sulphate, and returned to the furnace, when the temperature is gradually raised as before, and steam admitted when redness has been attained; the roasting being continued, accompanied with frequent babbling or stirring of the mass during from 8 to 14 hours, according to the richness of the ore. During this second stage, or "*goed roasting*," the ferrous sulphate added, as also the sulphates of iron, copper, etc., produced in the first roasting, suffer decomposition, the sulphuric anhydride (SO_3) evolved attacking the common salt, which, in the presence of steam, yields hydrochloric acid and sodic sulphate, thus—



the former (hydrochloric acid) in its turn decomposing the argentic sulphide with the production of argentic chloride. The steam in addition serves also, by its condensation in the condensing chambers through which the vapours pass in their course to the stack, to collect therin a considerable amount of silver, which would otherwise escape in a fine state of division into the atmosphere and be lost.

The roasted ore from the last operation is now subjected to the second operation or *lixiviation*, for which purpose a charge of about 4 cwt. is introduced into a row of wooden tubs or vats, each provided with a filter or false bottom. The contents of the vats are now exposed to the action of hot water, so long as a precipitate is formed in the escaping liquid, on the addition of sodic sulphide (Na_2S). By this treatment any sulphates or chlorides of copper, iron, nickel,

cobalt, zinc, etc., that may be present are dissolved out, with possibly a small proportion of silver salts; the metals of this solution being precipitated by the addition of lime-water, and subsequently smelted for their reduction.

The washed ore, after cooling, is transferred in quantities of about 2 cwt. to each of another series of tubs or vats, resembling in construction those described on p. 259, fig. 55, when a cold solution of *sodic hyposulphite* ($\text{Na}_2\text{S}_2\text{O}_3$) is conveyed from a reservoir and allowed to slowly percolate through the mass of materials, whereby it takes up the argentic chloride, producing a soluble double salt of sodium and silver, which filters through the bottom of the vessel into a trough, and is conveyed to the precipitating vats. The lixiviation with *sodic hyposulphite* generally lasts from 12 to 14 hours, according to the richness of the ore, being continued so long as a solution of *sodic sulphide* (Na_2S) shows the presence of silver in the filtrate.

The *precipitation* of the silver as argentic sulphide is conducted in vats holding from 40 to 80 gallons of the solution, and the precipitant (*sodic sulphide*), prepared by calcining a mixture of soda (soda-ash) and sulphur, and subsequently boiling the product with flowers of sulphur, is conveyed to the vats in stone jars, which are emptied into the vats, while a vigorous stirring is maintained during the addition. And it is necessary for the success of the process that sufficient *sodic sulphide* be added to separate the whole of the silver, while avoiding an excess of the precipitant, since the liquid filtered from this precipitate is again used in a subsequent lixiviation, and any excess of *sodic sulphide* present would cause a precipitate of argentic sulphide with a corresponding loss of silver. To determine the neutrality of the solution, small quantities are removed in test-tubes and tried with *sodic sulphide* and silver solutions respectively, a black precipitate by the former indicating a deficiency of *sodic sulphide*; while the absence of a precipitate, on the addition of the last named (*sodic sulphide*), with the production of a precipitate by the silver solution, added to a fresh trial, indicates that an excess of *sodic sulphide* has been added; to neutralise which, a further portion of the argentiferous liquid is added, until exact neutrality is attained.

The precipitated argentic sulphide is allowed to settle, and the supernatant liquid syphoned off and used again in the lixiviation of a subsequent charge of the roasted ore; while the dark brown precipitate collected on the bottoms of the vessels is washed with water for the separation of sodic sulphide, etc., then introduced into bags and pressed as dry as possible, when, after again washing and drying, it is ready for reduction.

The *reduction* of the dried argentic sulphide is effected by heating it in a muffle, when this compound suffers decomposition with the elimination of its sulphur; and the silver so separated only requires *refining* by *fusion*. For this purpose it is fused in graphite crucibles, along with metallic iron, by which treatment a regulus of iron rises to the surface and is skinned off, the complete absorption of the regulus being effected by projecting a mixture of bone-ash and wood ashes on to the surface of the metal, and then skimming off the scum, at which the silver remains of a fineness of from 980 to 985 parts in 100 and is cast into ingots for the use of the Mint.

126. Sulphuric Acid Process for Separating Gold and Silver from Copper.—This process has largely superseded the old method of liquation for the treatment of argentiferous copper-matts, or black-copper. For this treatment, the metal, containing an average of about 16 per cent. of silver, is first granulated and then introduced into a trough or tank lined with lead. The metal, introduced into the tank to a depth of about 3 feet, is now moistened by the addition of a small quantity of warm dilute sulphuric acid, and then exposed for a short time to atmospheric oxidation, by which the copper is oxidized and converted into cupric sulphate, while the gold and silver remain in the residue. After a short period of exposure, during which the copper loses its metallic lustre, a further quantity of warm dilute acid is added, until the surface of the metal again assumes its metallic appearance from the solution of the oxide previously formed on its surface, upon which it is again exposed to oxidation, followed by the further addition of dilute acid, and so on to the conclusion of the operation; the liquid running off through a hole in the bottom of the vats into troughs

lined with lead, in which, as the liquid cools, cupric sulphate separates by crystallization; while the gold and silver carried away in suspension, by the escaping liquids, is deposited in the bottom of the trough as a kind of mud.

The separation of the cupric sulphate from the mother liquor is further promoted by heating the liquid in leaden pans, heated by steam, when the acid liquor remaining is returned to the tank containing the copper, and used again for the solution of a further quantity of copper.

The mud collected from the gutters, as also from the boiling pans employed in the recrystallization of the cupric sulphate, and which contains the silver, along with any gold, is collected at intervals, and mixed with a proportion of litharge, so that the mixture on smelting will yield a lead containing about 2 per cent. of silver; which lead is then directly cupelled, and generally affords a silver containing from 1·5 to 1·7 per cent. of gold.

127. Claudet's Process for the Extraction of Silver.—This process has been recently applied to the extraction of the very small proportion of silver present in the copper liquors obtained in the treatment of Spanish, Portuguese, and other cuprous pyrites, by the wet methods of extracting copper.

The silver exists in these liquids as argentic chloride, dissolved in the excess of sodic chloride, with which the burnt pyrites was roasted prior to its lixiviation; and the silver is precipitated from this solution by the addition of a *soluble iodide*, such as a solution of kelp, the proportion of the iodide to be added being determined by a previous estimation of the amount of silver present in the liquors to be operated upon. The precipitated argentic iodide is accompanied by plumbic sulphate and chloride, along with subsalts of copper; when, after freeing from the last mentioned by treatment with dilute hydrochloric acid, the precipitate is treated with *metallic zinc*, by which the argentic iodide is decomposed, with the precipitation of the silver, along with some lead, etc., and the formation of zincic iodide, which salt may be subsequently employed to precipitate a fresh portion of argentic iodide from its chloride,

METHODS OF EXTRACTING SILVER BY CONCENTRATION WITH LEAD, AND SUBSEQUENT SEPARATION BY CUPELLATION.

The processes to be described under this head comprise the more ancient methods of extracting silver from argentiferous copper, cuprous products or copper ores from argentiferous blenders, native arsenic, nickel and cobalt ores, and would properly include the treatment of argentiferous galenas, the Pattinson process, etc. ; but the consideration of these latter processes are more conveniently treated under the metallurgy of lead. The method of concentration in lead is also applied to the treatment of silver ores such as occur in Norway, etc., in which the metal exists largely in the metallic state, when, by fusing such an ore with its own weight of lead, a highly argentiferous product is obtained, from which the silver is extracted by cupellation ; also auriferous raw copper containing silver is unfit for treatment by the amalgamation methods, since the gold would be mostly lost thereby, and such substances are accordingly better adapted for treatment with lead.

The argentiferous copper ores to be treated by the methods of concentration with lead, if rich in silver, but not containing sufficient lead, are first smelted in conjunction with galena (PbS) or with lead products; and the argentiferous matt so produced is desilverised by fusion with lead, when an alloy of lead and silver separates above a regulus of the sulphides of lead and other metals. Poorer ores are first smelted alone in the ordinary manner for the production of a matt, which is then treated with lead; and, similarly, argentiferous native arsenic, argentiferous nickel and cobalt ores, are previously smelted for the production of *speise* before treating them with lead for the concentration of the silver. The argentiferous lead obtained by either of these methods is either directly cupelled, or, if still too poor in silver, is further concentrated by the Pattinson process, and then subjected to cupellation.

The residues after treatment with lead, if from a copper ore, are smelted for the production of black-copper according to the practice of copper-smelting, when a further proportion of silver is sometimes extracted from the reduced copper by the *liquation* process.

128. Extraction of Silver by Liquation.—The method of concentration constituting the process known as "*liquation*" depends upon the fact that if argentiferous cuprous products be fused with lead or certain other easily fusible metals, then allowed to cool, and subsequently heated to a temperature above the melting point of lead, but below that of copper, then the lead alloyed with almost the whole of the silver will liquate or sweat out from the mass, and thus an argentiferous lead is obtained in which the silver may be, if necessary, still further concentrated by processes to be subsequently described, and from which the silver may be readily separated and refined by the process of cupellation; whilst there is left behind after liquation a mass of impure copper, retaining from .0008 per cent. to .003 per cent. of silver.

The process of liquation still pursued in the Hartz has, however, generally been superseded by one or other of the various *wet* methods of extraction, or by the European method of amalgamation. The copper concentrated to the condition of black or coarse copper is capable of profitable treatment by the method of liquation, only if it contain not less than about .03 per cent of silver. The black copper for liquation is reduced to fragments by breaking or hammering while hot, or it is crushed between rolls, and is

then melted in a small cupola furnace with lead or argentiferous litharge, in the proportion of 3 parts of copper, to 10 or 12 parts of lead, these being the ratios which give the best result. The alloy is then run from the furnace into iron moulds, forming it into discs of some 18 to 24 inches in diameter, and from 3 to $3\frac{1}{2}$ inches in thickness.

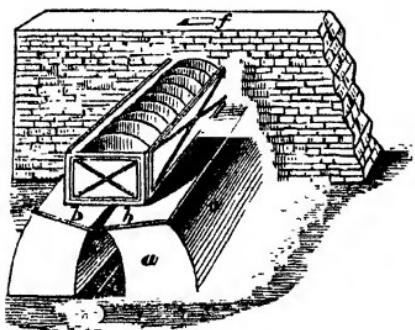


Fig. 58.—LIQUATION HEARTH EMPLOYED IN THE HARTZ.

These discs are then subjected to liquation by placing them as shown upon the *liquation hearth*, fig. 58, consisting of two walls *a*, *a*, inclining towards a median line,

each wall being surmounted by an iron plate *b*, *b*, leaving between their edges a longitudinal space of some 2 or 3 inches in width along the centre of the hearth. Between the two walls and beneath the longitudinal opening is a channel *c*, running the full length of the hearth, which collects the argentiferous lead as it liquates from the cakes, and conveys it to the receptacle or basin *d*. The discs of plumbiferous copper are placed as shown, resting in the angle formed by the two inclined planes *b* *b*, the spaces around and between the cakes being filled with charcoal. The sides of the cakes are now closed in, by placing iron plates against them, when a log of wood is introduced into the space *e*, between the walls, and ignited, by which, in forty or fifty minutes, the temperature has become sufficient to cause the rich lead to liquefy from the cakes; and it continues thus to liquefy and collect in the basin *d* during about two hours longer. The temperature is kept very moderate at first, until the largest proportion of the alloy has liquated out, when it becomes necessary to increase the heat by withdrawing the damper in the flue *f*, and adding more wood to the fire in *e*.

When lead ceases to flow from the cakes the fire is allowed to die out, and there remains a porous or spongy mass of copper, retaining usually from 10 to 20 or 25 per cent. of lead, with about .005 per cent. of silver. If richer than this it is again fused with lead and liquated for the extraction of a further proportion of the silver; or it is treated at once in a closed furnace containing a number of channels, and in which a higher temperature can be obtained than is attained on the liquation hearth; when the lead, largely oxidized to the state of litharge, and containing the silver along with oxide of copper, collects in the channels and is returned to the cupola with the next charge for the preparation of the discs or cakes for liquation. The copper after liquation is freed from lead, by the method of oxidation, upon the German hearth, fig. 12, as already described under copper; while the silver is extracted from the rich lead by cupellation.

129. Cupellation.—When lead is fused in an oxidizing atmosphere it is rapidly converted into the fusible plumbic oxide or litharge (PbO); and the fused litharge has further the property of rapidly dissolving oxides of other metals, as

copper, antimony, bismuth, zinc, tin, etc., some of which, as the two latter, are either infusible, or fusible only with difficulty when treated alone; while silver is not oxidized by the treatment, either when heated alone or when melted in conjunction with lead. So that in this manner, if an alloy of silver with lead and smaller proportions of other metals be suitably heated to fusion in a blast of atmospheric air, the lead and other oxidizable metals are converted into fluid oxides, which, as being lighter than the molten metal, float on its surface and collect around the edges of the fused metal, from whence they are removed, and are again and again replaced until the whole of the baser metals have been thus removed, when the silver is left freed from the greater portion of its impurities. This process of separating oxidizable metals from silver by the joint action of *heat* and *air* constitutes the process of *cupellation*, which, on the large scale, is conducted upon the hearth of a kind of reverberatory furnace, of which the bed is formed of a material as *bone-ash*, *marl*, or other like substance which is *not corroded* under the influence of molten litharge; such a bed or hearth being known in England as a *test* or *cupel*. And from the surface of the test the molten litharge is run off into receptacles placed to receive it.

Cupellation on the large scale is mostly conducted after one of two methods, known as the *English* and *German* methods respectively, which differ only in the details of the construction of the furnace employed and mode of charging the argentiferous lead. In the first named the hearth or *test* is formed of *bone-ashes*, is *movable*, of *smaller capacity* than the German hearth, and the charge of lead is only added in *successive portions* after that previously added has been converted into litharge, and the *roof* of the furnace is *fixed*; while the hearth of the German furnace is constructed of a *calcareous marl*, and unlike the English furnace has a *movable roof* and a *fixed bed* of considerably larger dimensions than is adopted in England; whilst the charge of lead is often, though not always, wholly added at the commencement of the operation.

130. English Method of Cupellation or Refining of Silver.—This process is conducted, as already stated, in a kind of reverberatory furnace, figs. 59 and 60. The movable

hearth or *test* *a*, is formed of an ellipsoidal ring *b*, of wrought iron, of from 2 feet 6 inches to 5 feet in major diameter, and from 1 foot 6 inches to 3 feet in minor diameter, to the lower edge of which is rivetted four or more flat bars of iron as shown, fig. 61. Into this open frame is rammed a quantity of finely-powdered *bone-ashes* moistened with a solution of *pearl-ashes* sufficient to make the powder slightly cohesive;

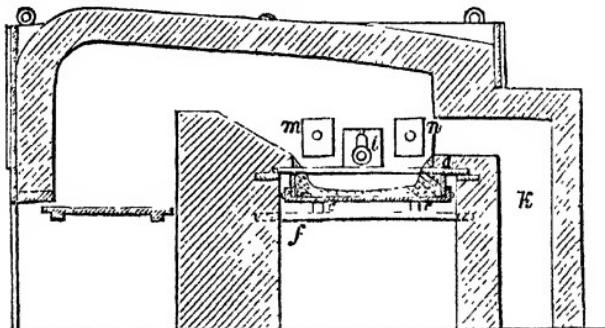


Fig. 59.—VERTICAL SECTION OF THE ENGLISH CUPELLATION FURNACE.

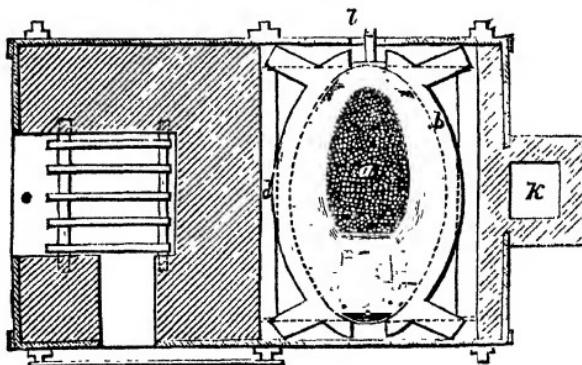


Fig. 60.—HORIZONTAL SECTION OR PLAN OF THE ENGLISH CUPELLATION FURNACE.

and the cavity *c* of the form shown, fig. 62, is then scooped out so as to incline gently from all parts towards the centre, where it is only about one inch in thickness; and by drilling a hole from the under side the enriched lead may be thereby.

tapped out. The test so prepared is introduced from beneath, placed in contact with the *compass ring d*, fig. 59, of wrought iron, and supported in this position by the four iron wedges *e*, *e*, driven in between the bottom of the test and the two iron bars *f*, *f*, placed across the chamber beneath the test, and built into the side walls; while in other furnaces the test is supported against the compass-ring upon a carriage or tram by which it can be run in and out. The front portion

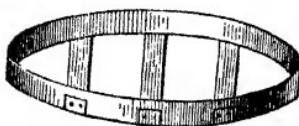


Fig. 61.—TEST-FRAME.

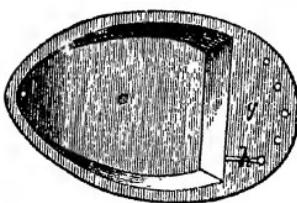


Fig. 62.—PLAN OF TEST.



Fig. 63.—VERTICAL SECTION OF TEST.

surface of the molten metal at *l*, and at each side of the twyer opening are apertures, *m*, *m*, which serve for the introduction of the pigs of lead as the operation proceeds. A jet of steam is introduced into the flue *z*, to condense any fume passing over from the hearth.

The process of cupellation comprises two stages. In the first or *concentration stage* the operation is continued until the lead contains from 200 oz. to 250 oz. of silver per ton of metal, when it is tapped out, and the operation subsequently resumed upon this concentrated metal, for the separation of the lead, etc., as completely as possible.

(*g*) of the test, figs. 62 and 63, is known as the *breast*, and in it is made a channel *h*, communicating with the hollow of the test and a hole passing through the breast, by which means the melted litharge is drawn off from the test during the process; while, as this channel becomes corroded, and too much increased in size thereby, it is stopped and another one is made at *h'*, which in its turn is replaced by *h''*. The flue end of the hearth or test communicates by two openings with the downward flue *k*, which leads by an underground culvert to a high stack. The atmospheric blast, driven in either by a fan or by a steam jet, is introduced to the

Before commencing to cupel upon a new test, the latter is thoroughly dried by some weeks of exposure to the warm atmosphere of the furnace-room; and, after fixing in its position, the fire is lighted, and the temperature very gradually raised so as not to crack the cupel. When the heat approaches to dark redness, the argentiferous lead previously melted in a kettle attached to the furnace is ladled on to the hearth or test, and the temperature is increased to bright redness, or a little above the melting point of litharge, when the blast is let on and oxidation proceeds regularly and rapidly. The litharge, as it collects, passes by the channel *h* to the hole already mentioned through the breast of the test, and so from the surface of the test into the pot placed for its reception in the vault beneath. As the operation proceeds, attended with the removal of the lead as litharge, more pigs of lead are introduced through the openings *m*, *m*, so as to maintain a charge of from 500 to 600 lbs. always upon the hearth, until the whole charge ranging from 5 to 15 tons, according to the size of the test, has been introduced, the process being then continued, until in about twenty hours from the commencement, the charge of lead upon the test has acquired the degree of concentration above stated, when a hole is drilled through the bottom of the test at its lowest point, and the charge drawn off into a cast-iron pot placed upon wheels in the vault beneath, from which it is ladled out into pigs. The hole is then plugged up with bone-ash, and the process of concentration resumed upon another charge.

The second stage of the process, which might be designated as the *refining*, is conducted on a fresh test, and operates upon the concentrated lead of the last operation after the manner described for the previous stage, except that the charge of concentrated lead worked off at each charge is only from $2\frac{1}{2}$ to 3 tons, and that the litharge from this step should be kept separate, as being more highly argentiferous than that produced in the first stage; whilst the temperature towards the close of the operation should be increased so as to prevent the solidification of the silver before the whole of the lead has been removed in the form of litharge. The operation is continued until, when on slightly lowering the temperature of the furnace, impurities cease to rise to the surface of the

molten silver, thus indicating that the metal has attained the necessary degree of fineness, which, on the average, will be about 998 parts of silver per 1000. The cake of silver is then allowed to cool and solidify on the test; when, as the surface of the metal solidifies, the phenomenon of *spitting* occurs, by which the surface is thrown up into a number of protuberances or crater-like asperities, due to the escape of occluded oxygen, and which, without care in the cooling, would be attended with considerable loss of silver. The cake when cold will weigh from 5000 to 7000 oz. It is readily detached from the bottom of the test, and after cleaning from adherent matter, it is cut up, remelted, and cast into ingots.

The substance of the test absorbs a considerable proportion of litharge, for the recovery of which it is broken up and introduced along with the other materials of the furnace charge in the process of lead smelting.

The loss of lead in the English method of cupellation amounts to about 5 per cent.

131. German Method of Cupellation.—This process, the product of which is an impure silver called "*Blicksilber*," containing about 94 per cent. of silver, accompanied chiefly by lead and smaller proportions of copper, nickel, cobalt, arsenic, etc., is conducted in a kind of reverberatory furnace, but without stack or chimney, the products of combustion escaping through an opening *g*, opposite the fire-bridge, which opening serves also for the introduction of the lead; while the fireplace is much smaller in proportion to the hearth than in the English furnace. The roof is usually formed of a movable iron cover *a*, made of plates rivetted together, and coated over its interior with clay, or with loam and hair. The roof may be lifted off and swung around by a crane at the side of the furnace, so as to allow of the withdrawal of the cake of silver and the cooling or repair of the hearth. At one side of the hearth is situated a pair of inclined twyers, *b*, *b*, controlled by suitable valves, and which direct the blast towards the middle of the hearth, so as to cause the litharge to flow from the surface of the metal towards an opening *c*, in the angle near the fireplace, through which the litharge is withdrawn, and the progress of the cupellation observed. The hearth itself, which is here fixed, while in the English furnace it is made

movable, is circular, of some 8 or 10 feet in diameter, and composed of a natural calcareous marl, or, when such cannot be obtained, then a mixture of calcic carbonate and clay with a little ferric oxide is substituted. The bottom is usually formed by first introducing upon the brickwork a layer (*d*)

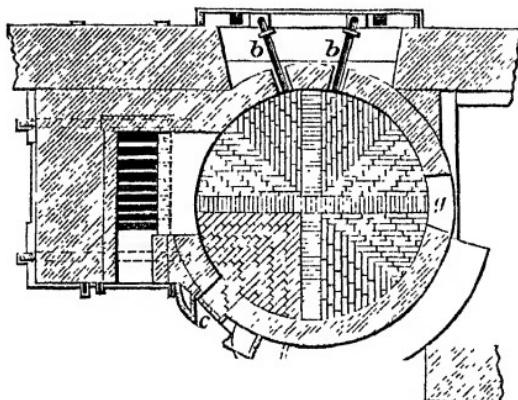


Fig. 64.—PLAN OF THE BED OF THE GERMAN CUPELLATION FURNACE.

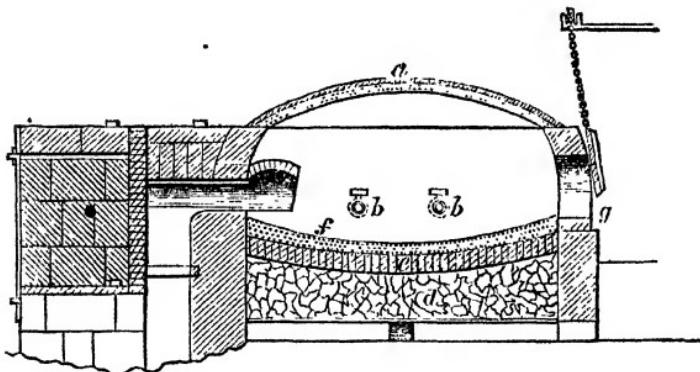


Fig. 65.—VERTICAL SECTION OF THE GERMAN CUPELLATION FURNACE.

of slags from the lead-smelting furnace, upon which is laid a concave brick bottom *e*; and upon this latter the moistened marl, *f*, is well rammed, the marl being prepared by stamping or grinding it to a fine powder, passing it through a sieve

and then mixing it with a proportion of old hearths also ground and sifted; after which the mixture is allowed to stand some time, and then is thoroughly kneaded until it will cohere well together when squeezed in the hand, in which condition it is well rammed into the hearth to the proper form required, considerable importance being attached to the degree of concavity given to the bed as influencing the rapidity and completeness of the cupellation. The layer of marl requires repairing or renewing after the cupellation of each charge. The masonry of the furnace is well cramped together by iron tie-rods, and is traversed by passages for conveying away the moisture produced during the cupellation.

After the preparation of the hearth, pigs of the argentiferous lead, to the extent of about one-third of the total charge, are carefully introduced on to the hearth; a former practice, now generally discontinued, being to place a layer of straw beneath them to prevent injury to the hearth. The lead having been thus introduced, a wood fire is made upon them, and the cover of the furnace swung by the crane into its position and luted down, after which a fire, burning wood as the fuel, is made upon the grate, and the temperature raised so as to melt the lead and maintain it only at about a dull or dark red heat. During this period, or melting down, constituting the *first stage* of the operation, a dark coloured, heterogeneous, pasty mixture of the oxides of lead, copper, iron, zinc, antimony, and other foreign metals, with sulphides of these metals, accompanied by earthy matters and some metallic lead, rises to the surface, constituting a scum called by the Germans "*Abzug*." As the abzug collects, it is raked out at the door *c*, in the corner of the hearth near the fire-bridge. This stage usually lasts from three to four hours; but much depends upon the purity of the lead operated upon. Towards the conclusion of this stage the metallic bath exhibits a clear metallic surface, upon which the temperature is raised and the blast let full on, when in from one to two hours afterwards, the bath of metal has acquired a peculiar circular movement, and there rises to the surface a more fluid and purer product than the abzug. This product, known as "*Abstrich*," is an impure litharge, containing from 60 to 90 per cent. of plumbic oxide (PbO), the remainder consisting of the oxides of antimony,

arsenic, copper, iron, and zinc in varying proportions, with occasionally also considerable proportions of earthy matters derived from the bottom of the cupel. The abstrich is allowed to flow through channels cut across the breast in the corner of the furnace in the manner already described under the English method of cupellation, the heat being raised sufficiently high to maintain the fluidity of the abstrich that it may flow away from the hearth readily. The formation of abstrich constitutes the second stage of the process.

Of late only refined and purer leads are treated in the cupellation, and then no abstrich is formed (Plattner), but only a small proportion of abzug, which is succeeded by the litharge proper, which constitutes the *third stage* in the order named above.

It is after the third or *litharge stage* has commenced that the remainder of the charge of lead is gradually added to the furnace, the pigs of lead being so placed in the furnace that the lead liquates from them, and flows down into the bath of metal on the hearth, leaving a more refractory abzug above, unmixed with the metal. The litharge, as it forms, is run off through the channels in the breast already mentioned, new ones being made as the previous ones become too deep, or become stopped through any cause, and the litharge is collected in large vessels and allowed to cool slowly; when, with the exception of that portion collected towards the end of the process, and which is richer in silver, requiring a separate reduction and cupellation for its extraction, the litharge so obtained is sent into commerce as *red* or *yellow* litharge, varieties chiefly depending upon its mode of cooling.

As the litharge period approaches completion, the temperature requires to be raised to maintain the fluidity of the silver as the lead is gradually removed; and the layer of litharge on the surface of the metal becomes gradually thinner, appearing in the latter stages only as a cloud, and eventually clearing off and exposing the bright metallic surface of the silver, a phenomenon constituting the "*blick*" of the Germans; at the same time the metal which was previously in motion has become motionless. The blast is now turned off, and water is thrown upon the fire and on to the hearth in order to harden the cake of "*Blicksilber*," which is subsequently withdrawn

from the furnace and freed from marl, litharge, and other adherent matters, when it is ready for *refining* in small reverberatory furnaces for the production of fine, or according to the Germans, "*Brandsilber*."

In a furnace of the dimensions described, from 10 to 15 tons of lead may be treated during one cupellation, lasting from seventy-five to eighty hours; while the loss of lead amounts to from 8 to 10 per cent.

The German furnace, as adapted to the consumption of *coal* instead of wood, does not differ materially from the furnace last described, except that the hood is made somewhat higher; and, as employed at Tarnowitz in Upper Silesia, the bed is formed of a mixture of dolomite (carbonate of lime and magnesia) and fire-clay, rammed as before into the form of a concave bed, while the vapours or fumes from the bed either escape directly into a stack at the end of the bed opposite the grate, or are first directed, according to the stage of the operation, through a series of subterranean condensing chambers before entering the stack; and the blast is supplied through one semicircular twyer nozzle; but the process is otherwise essentially the same as that already described.

The rich lead produced by smelting galena in the Swedish blast or ore furnace contains an average of about 280 oz. of silver per ton, and is accordingly at once cupelled according to the German method, an operation at first attended with the production of a *black litharge*, containing antimony, zinc, copper, etc., which is succeeded by a purer yellow litharge; while the resulting cake of metal obtained still retains some lead and is *refined* as described in the subsequent article, in a smaller furnace supplied with blast by a pair of tuyers, the hearth or test of which also contains, in addition to limestone and clay, a certain proportion of bone-ashes.

REFINING OF SILVER.

The metal, as produced by the various plans of amalgamation, by precipitation (the wet methods), or by the concentration methods last described, usually retains sensible proportions of foreign bodies, as copper, lead, antimony,

arsenic, bismuth, nickel, zinc, or sulphur, according to the mode of its extraction, all of which, with the exception of copper, materially impair the malleability of the silver, and render it unfit for the purposes of coinage or other uses to which it is applied; and for the further and more complete elimination of these elements, the silver is submitted to the refining operation—a process conducted either upon a *test* or *large cupel* formed of a material like bone-ash, which is capable of *absorbing* molten litharge while resisting its corrosive action, and which test forms the bottom or hearth of a reverberatory furnace—or the refining is effected by fusing the silver in crucibles. Whichever method is pursued, the object is to oxidize the impurities by exposing them at a temperature above the melting point of silver, to a blast of atmospheric air exactly as described under the process of cupellation, except that, instead of removing and collecting the litharge and other oxidized products from the surface of the fused metal, the material of the hearth is such as to absorb these substances as they are formed.

132. Refining Silver upon a Test or Cupel.—This process is exactly analogous to the English process of cupellation, except that smaller quantities are operated upon, whereby an economy in fuel is effected, and the process is also conducted without blast; while, as above, the litharge is wholly absorbed by the substance of the cupel, instead of being drawn off over the breast of the furnace.

For the purification of the “*Blicksilber*” produced in the German cupellation, the refining is effected upon a test formed of marl and supported in an iron bowl, the operation being the same in principle as the original cupellation. The *blicksilber* is introduced into the test, which is heated by charcoal placed around it, and the blast is turned on, when in from one and a half to two hours the metal is fused; and from time to time afterwards the fluid metal is stirred with an iron rod so as to more thoroughly expose all portions to the oxidizing influence of the air, the litharge as it forms being absorbed by the material of the test. The operation is continued until a drop of the metal, withdrawn on the end of an iron rod, presents a surface free from spots,* while on

* Percy.; Vol. III.

cooling it assumes the pure white colour of silver, and also presents, as the metal solidifies, the phenomenon known as *spitting*. The process continues altogether from three to four hours, when the fire is withdrawn and the silver either allowed to cool very gradually, or is solidified by projecting warm water upon its surface, when it is extracted, and requires only to be freed from mechanically adhering impurities to prepare it for sale.

Brandsilber, or fine silver, could be produced at once in the first cupellation for *blicksilber*; but it is found more economical to subject it to this second cupellation or refining on a smaller hearth, since the large size of the hearth employed in the first process, and the rather high temperature required for the latter stages of the refining, involve a considerable increase in the consumption of fuel; while also the litharge produced in the final stage carries with it a considerable proportion of silver, and it is accordingly desirable to collect this and smelt it separately for the recovery of the silver.

CHAPTER VI.

GOLD.

133. Physical and Chemical Qualities.—Gold, as seen in the mass, is the only yellow metal; but as viewed by transmitted light, after reducing the metal to extreme thinness, it appears to possess a greenish tint, changing to red when heated (Faraday); while when in a fine state of division, as when precipitated from its solution by the addition of ferrous sulphate, or by the metals iron, zinc, copper, etc., it has a dull brown colour, and is void of metallic lustre; but the particles of the pulverulent metal can be *welded* together in the cold by the application of pressure, with subsequent hammering, or by hammering at a dull red heat, when the solidified metal is capable of receiving a high polish. The *native* metal crystallises in cubes and other forms of the monometric system, and specimens of the metal can also be obtained crystallised after fusion. Gold is malleable and ductile in the highest degree, leaves of the metal being produced not exceeding $\frac{1}{282000}$ th part of an inch in thickness, or such that an area of 56 square inches of the leaf will only weigh 1 grain; whilst its ductility is such that a wire can be drawn so that a length of 500 feet does not exceed 1 grain in weight; but the malleability and ductility of the metal are materially influenced by the presence of only small proportions of foreign metals, as antimony, arsenic, tin, lead, etc., as noted under the alloys of the metal. It is a good conductor of heat and electricity, though in these respects it is much inferior to silver.

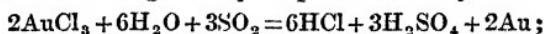
Pure gold is almost as soft as lead, being inferior to either copper or silver in hardness; and hence the necessity of hardening this metal by alloying it with copper, etc., for the purposes of coinage, jewellery, and other uses where it is exposed to much wear. It is not acted upon by atmospheric air, either at ordinary temperatures or when strongly heated;

neither is it tarnished by exposure to the action of sulphurated hydrogen. The melting point of this metal is given by Pouillet as 1200°C . (2192°F .), while Daniel gives it as 1425°C . (2596°F .). It expands considerably on fusion, and though practically fixed it is slightly volatilised at very high temperatures, as in the focus of a powerful lens; also, when alloyed with silver, a small proportion of gold along with the silver is volatilised by continued exposure to furnace temperatures. The specific gravity of gold ranges from 19.25 to 19.5, according to the mechanical treatment it has received. A gold plate prepared from fine gold, precipitated from its chloride by means of oxalic acid, had a specific gravity of 19.2945,* which became, after once passing through the rolls, 19.2982 (Rigg), and with the exception of platinum it forms the heaviest known body. Its specific heat is .324 (Regnault).

Gold is not acted upon by nitric, hydrochloric, sulphuric, or any single acid except the selenic, but it is dissolved by chlorine, or an acid mixture as the nitro-hydrochloric acid (aqua-regia), which evolves chlorine, yielding under these circumstances a solution of auric chloride (AuCl_3). Bromine also attacks gold even in the cold, whilst iodine has an exceedingly feeble action upon it. Sulphur is without action upon gold at any temperature, although double sulphides of gold and the alkalies are readily produced by fusing the metal with an alkaline sulphide. The oxides and sulphides of gold are reduced to the metallic state by the simple application of heat, and the metal is precipitated from its chloride by phosphorus, sulphur, sulphurous anhydride, ferrous salts, arseniuretted or antimoniuuretted hydrogen, arsenious and antimoniuous chlorides; by most metals, as iron, copper, zinc, bismuth, etc., and many vegetable or animal substances. The method of precipitating gold from its pure chloride by the addition of sulphurous anhydride, oxalic acid, or ferrous sulphate, is employed for the preparation of pure or standard gold; and for this purpose the pure gold, as extracted by the ordinary metallurgical methods, is dissolved in nitric acid, evaporated slowly to expel all excess of nitric acid, then largely diluted with water and allowed to stand or settle for about a week, by which any argentic or argentous chloride will sub-

* *Journal, Chemical Society.* 1874.

side; then to the clear decanted or filtered liquid, one of the last named reagents, preferably sulphurous anhydride or oxalic acid, is added. If sulphurous anhydride be employed, the gas is passed through the solution kept cold until saturation, when metallic gold is precipitated slowly—



and after boiling in pure hydrochloric acid, with again washing and drying, it is fused with hydric-dipotassic sulphate and borax, when gold having a fineness of 9998 parts in 10,000, will be obtained.

Gold imparts to glass a beautiful ruby red colour, the metal existing in the metallic state in glass so coloured. The atomic weight of gold is 196·6, and its chemical symbol is Au.

Commercial gold is never absolutely pure, but the degree of its purity or *standard* is very uniform for the metal derived from the same locality; while the standard of gold imported from the various gold mining districts varies much, as also does the nature of some of the foreign metals accompanying it; but silver is invariably present in the commercial metal. Californian gold is thus of much lower standard than that derived from Australia; for whereas the former ranges between 865 to 930 parts of gold per 1000, or more usually between 865 and 890 parts per 1000, the standard of Australian gold is from 930 to 980 parts per 1000; and both varieties are usually associated with copper and iron, whilst Australian gold is frequently rendered brittle from the presence of small proportions of lead and antimony. The following analyses show the composition of native gold received from different mining districts:—

ANALYSIS OF NATIVE GOLD.

LOCALITY.	AUSTRALIA.		CALIFORNIA.		WALES.	RUSSIA.	AFRICA.		TRANS-	VANIA.	PERU.
ANALYST.	Henry.	Makins.	Lercl.	Rivot.	Forbes.	Rose.	Henry.	Rose.			Forbes.
Gold,	956·8	946·4	927·0	891·0	898·3	989·6	982·5	604·9	974·6		
Silver,	39·2	49·5	69·0	105·0	92·4	1·6	111·7	387·4	25·4		
Copper,	4·1	4·0	0·5	1·0		
Iron,	1·6	4·1	..	2·0	trace.	3·5	3·6		

134. Carat and Standard.—*Fine* or perfectly *pure* gold is described as 24 *carat fine*, the pound or 1000 parts being divided into 24 carats, and different alloys of gold are spoken of as being so many carats and grains fine, according to the amount of gold present in them (4 carat grains being equal to 1 carat). The English gold coinage, or *standard gold*, consisting of 11 parts of gold to 1 of copper, or in 24 parts containing 22 of gold with 2 of copper, is accordingly described as 22 carat fine. The standard still employed by goldsmiths, however, though of 22 carat fine, contains in the 24 carats 22 of gold with 1 of copper and 1 of silver. Thus the statement that an alloy is *better* or *worse* by so many carats and grains, expresses that the given alloy contains so many carats and grains, more or less respectively, than the *standard*, which, as already stated, is 22 carat fine.

The fineness of any specimen of gold or gold alloy can only be accurately determined by a properly conducted analysis, or as it is termed *assay*, in which the gold is separated in an absolutely pure state, and then carefully weighed; but for many purposes of commerce, where copper forms the chief alloying metal, recourse was formerly had to the more quick and ready, yet with good judgment, fairly accurate method of the *touchstone*, by which an approximation to the fineness of the alloy was determined by the comparison of streak produced by the alloy, with that produced by specimens (needles) of definite and known composition, a further comparison of the streak being made by treating them with nitric acid.

The *touchstone* is a dark basaltic stone, originally obtained from Lydia, but now obtained from Bohemia, Saxony, Silesia, etc., its surface being prepared and left so that it will just abrade the metal from a sharp angle of the alloy, when such is drawn over the stone; and for the purposes of assay, a number of needles of alloys of definite composition are prepared, and comparison between these and the alloy under examination is made by drawing each of them across the stone once or twice, and then treating the streak or abraded metal so left on the stone, with nitric acid of a specific gravity of about 1·2, when the streak from the less pure alloy will be more readily acted upon, with the production of a more or less green colour, according to the proportion of copper present; and

the valuation is made by determining to which of the test-samples the streak most nearly corresponds, when the fineness is reported accordingly. This process, although abandoned for accurate assays, is still used occasionally for the approximate assay of small articles of jewellery, from which specimens cannot be taken for a correct assay, and also it is of use to the assayer in determining the approximate fineness of the gold, that he may more readily regulate the amount of lead required in the cupellation of the alloy.

135. Gold-beating.—For the manufacture of the gold leaf used for gilding and other purposes, the metal is first fused under borax and cast into small ingots, each weighing about 2 oz., and which are then hammered to a thickness of $\frac{1}{6}$ th of an inch, after which the metal is rolled, until a ribbon is produced having a thickness of about $\frac{1}{300}$ th of an inch, the gold requiring frequent annealing during this operation. The ribbon is then cut into portions of 1 inch square, about 150 of which are placed upon the top of each other, with a thickness of a specially prepared tough paper, placed between each pair of small plates, and the whole is made into a packet by two bands of parchment passed around the pile; the packet so prepared being hammered for about thirty minutes upon a solidly fixed marble block or anvil with a hammer having a slightly convex face, and weighing about 15 lbs., by which treatment the sheets are increased from 1 inch square to about 4 inches square, or sixteen times the original area. These sheets or leaves, in their turn, are each cut into four, and the pieces so obtained placed together into a packet, as before, except that, instead of paper, a layer of a fine membrane known as *gold-beater's skin*, prepared from the peritoneal or serous coat of the intestines of the ox, is placed between each sheet, and the packet is enclosed in parchment, the beating being continued as before, under hammers not quite so heavy as the former; when, after two hours' hammering, the sheets are again cut up into squares, rearranged as before, and the operation of beating repeated, until the leaves have acquired the degree of tenuity required for the purposes to which they are to be applied; and which tenuity can be carried to the limit previously noted, or so that a sheet of gold leaf of 4 inches square will scarcely exceed 1 grain in weight.

136. Gold and Oxygen.—The affinity between these elements is only very feeble; and the oxides formed by their union are very unstable, undergoing decomposition under the influence of heat alone, or by exposure to sunlight, while they have but little tendency to combine with oxygen acids, being rather chlorous than basylous in their chemical relations.

Aurous oxide (Au_2O) is an unstable body, precipitated as a dark-green precipitate on the addition of a dilute cold solution of potash to a solution of auric chloride, being careful to keep the latter in excess. It is decomposed in an excess of potash, with the production of auric oxide and metallic gold; hydrochloric acid likewise converts it into auric chloride and metallic gold.

Auric oxide (Au_2O_3) is obtained by first treating a solution of auric chloride with an excess of potash solution, by which the aurous oxide and oxychloride first precipitated are redissolved in the alkaline solution; then by boiling this brown solution for about fifteen minutes a potassic aurate results, and the solution becomes yellow in colour. It is now treated with sulphuric acid in slight excess, by which auric oxide is precipitated, which requires careful washing to separate the last traces of sulphuric acid; besides which it retains small traces of potash, and for the separation of the latter it requires treatment with a strong solution of nitric acid. Auric oxide, after dessication at a temperature of $100^\circ\text{C}.$, exists either as a brownish-black powder, or as a brown mass possessing a conchoidal fracture. It is decomposed, as already noted, with the separation of metallic gold, upon the application of a red heat, or by exposure to sunlight. It is dissolved by hydrochloric, nitric, or sulphuric acid; but its solutions in the two latter acids are decomposed on the addition of water, with the reprecipitation of the auric oxide; and with alkaline bases it yields a class of colourless salts known as aurates.

137. Gold and Sulphur.—The union of these elements cannot be effected by the influence of heat, and it is doubtful whether any combination of these elements exists native; but two sulphides corresponding to the oxides can be formed by wet methods.

Aurous sulphide (Au_2S) is precipitated as a dark brown

or black precipitate, when sulphuretted hydrogen (SH_2) is passed into a *boiling* solution of auric chloride (AuCl_3).

Auric sulphide (Au_2S_3) is deposited as a flocculent yellow precipitate when sulphuretted hydrogen is passed through a cold dilute solution of auric chloride, its colour becoming deeper on dessication. It is soluble in alkaline sulphides, especially the polysulphides; and it suffers decomposition with loss of its sulphur, if heated to dull redness, upon which property is based one of the wet methods, to be subsequently described, for the extraction of the metal, according to which the gold is extracted from the ore by treating it with chlorine water, and the metal precipitated from this solution by sulphuretted hydrogen, when the auric sulphide is subsequently decomposed by heat.

138. Gold and Chlorine.—Chlorine constitutes the best solvent for gold, with which it forms two compounds, the most important of which, *auric chloride* (AuCl_3), results when gold is treated with nitro-hydrochloric acid, when it yields a yellow acid solution, which, if neutral, becomes of a deep red colour; the latter being obtained on evaporating the acid solution until chlorine begins to be evolved, when a dark red crystalline mass, deliquescent in the air, results. The neutral auric chloride also results when aurous chloride (AuCl) is decomposed by water. The acid solution of this salt (auric chloride) slowly deposits metallic gold when exposed to sunlight; metallic gold is also precipitated from this solution by phosphorus, ferrous salts, arsenious and antimonious acids, by many metals, by potassic oxalate, many vegetable and animal substances, tincture of galls, etc. Stannous chloride forms a most delicate test for auric chloride, sufficing to detect 1 part of gold dissolved in over 60,000 parts of liquid, this reagent precipitating the purple or brown coloured precipitate (purple of Cassius) according to the strength of the solutions, etc.; while for the production of the purple precipitate a mixture of stannous and stannic chlorides is preferable, since pure stannous chloride always precipitates the brown compound.

The peculiar compound, "*Purple of Cassius*," containing oxide of tin and metallic gold, is of doubtful and uncertain composition. It is unacted upon by hydrochloric acid; but

boiling nitric or sulphuric acid improves its colour, and dissolves out any stannic oxide. It is also insoluble in solutions of potash or soda; but the unignited product is soluble in ammonia, yielding a purple liquid from which the colouring matter very slowly but gradually separates. It is largely employed as a material for imparting tints, varying from flesh to a deep or ruby red colour, to porcelain and glass goods; and the product has become, accordingly, an object of manufacture in the arts, for which purpose it can be obtained in a variety of ways, as by the addition of a carefully prepared mixture of stannous and stannic chlorides to a solution of auric chloride, made as neutral as possible. Another method (Makin) consists in the preparation of the tin solution by adding to a dilute solution of ferric chloride (Fe_2Cl_6) the solution of stannous chloride, until the former changes from yellow to green, or from a ferric to a ferrous salt, when the solution is diluted to twice its bulk (the ferrous salt does not interfere with the process). This solution is then added to a solution of the neutral auric chloride, containing about 1 part of gold in 360 of water, the mixture being well stirred during the addition of the stannous salt and the precipitation of the purple of Cassius; the latter now only requires to be washed quickly by decantation and then carefully dried to fit it for use. This purple compound can be produced in the dry way by melting together $2\frac{1}{2}$ parts of gold with $3\frac{1}{2}$ of tin and 15 parts of silver, the whole being fused under borax to prevent the oxidation of the tin; when the product so obtained, after treatment with nitric acid to dissolve out the silver, leaves the purple compound containing gold and tin.

139. Gold and Phosphorus. — Gold and phosphorus unite readily under the influence of heat, yielding a yellow phosphide more fusible than gold. In the wet methods, phosphuretted hydrogen passed into a solution of a salt of gold precipitates metallic gold; but on continuing to pass the gas the precipitate changes to a black non-metallic mass containing phosphorus.

140. Alloys of Gold. — Pure gold is too soft for direct application to the purposes of jewellery, coinage, etc., and accordingly for these purposes it is alloyed with variable

proportions of copper and silver; its alloys with these metals constituting its most important applications, although gold is capable of alloying with almost any of the metals.

Copper increases the hardness and brightens the colour of the gold with which it is alloyed, the maximum of hardness being attained when the copper constitutes one-eighth of the alloy. The alloys have a greater volume than that of the constituents, and are more fusible than pure gold. If pure copper be employed in the mixture, the malleability of the alloy is scarcely inferior to that of pure gold; but traces of antimony, arsenic, tin, or lead in the copper impairs materially both the ductility and malleability of the metal, and even renders it quite brittle; while the presence of silver together with copper impairs in a lesser degree the malleability of the alloy. Goldsmiths in England adopt two standards for these alloys of copper and gold, the lower one, known as the 18 carat standard, is used for jewellery, except wedding-rings; whilst the higher one, or 22 carat standard, established by Henry VIII., is the one employed for the British coinage, and corresponds to 11 parts of gold with 1 of alloy, or in 1000 parts of 916·66 of gold to 83·33 of alloy. In France and the United States the standard for gold coinage consists of 900 parts of gold with 100 of copper.

The *solder* employed for uniting the different parts of ornamental gold articles consists of 5 parts of gold and 1 of copper; or sometimes silver is added in addition, when the proportions are 4 parts of gold, 1 of silver, and 1 of copper, the effect of silver being to impart a lighter colour to alloys of gold and copper.

The various shades in colour of the *gold leaf*, *Dutch leaf*, and other foils occurring in commerce, are obtained by alloying gold with varying proportions of copper, or of copper and silver. Thus, with from 30 to 32 per cent. of copper, the leaf has a reddish colour; while silver produces a series of pale-green shades, until, with about 50 per cent. of this metal, the alloy is almost white, and intermediate shades of colour are obtained by alloying the gold with from 25 to 40 per cent. of copper, and 12 to 16 per cent. of silver.

Gold and silver unite in all proportions when melted together, the resulting alloys ranging in colour from almost

the whiteness of silver, through greenish-white, greenish-yellow, and orange, to the yellow colour of pure gold, one-twentieth of silver added to gold materially affecting its colour; thus the alloy, consisting of equal parts of the two metals, possesses an almost silver whiteness; while 3 parts of silver to 7 of gold produces an alloy of a green colour. The effect of silver is to harden the gold without impairing its malleability, while sensibly reducing the melting point of the metal. All native gold, especially Californian varieties, contains more or less silver; and the alloy added to the pure gold in the manufacture of the old English guineas consisted of equal parts of copper and silver, the result being an alloy possessed of very considerable hardness.

Gold and mercury unite readily, with the formation of a white amalgam, from which the mercury can be again separated by distillation. If the gold be in a fine state of division it is quickly dissolved by mercury even in the cold; but if the mixture be slightly heated, the amalgamation is much more rapid, the mercury taking up a considerable proportion of gold without losing its liquidity. The amalgam of two parts of gold to one of mercury is white in colour and of a pasty consistency; and a solid amalgam, having a composition represented by the formula Au_2Hg , obtained in four-sided prisms, has been described by Henry.

Gold and lead alloy readily; but small proportions of lead suffice to impair the ductility of gold, even rendering it quite brittle, and generally useless for any of the applications to which gold is applied; even $\frac{1}{1520}$ of lead renders gold less ductile, and impairs its coining qualities (Hatchet).

Antimony is particularly destructive to the malleability of gold, quantities not exceeding .05 per cent. impairing its malleability; while .5 per cent. of antimony in gold renders it brittle.

Gold and tin form alloys which, if the tin be quite pure, are malleable, of a paler colour than gold, while their specific gravities are in excess of the mean of their constituents.

Zinc may be alloyed with gold, yielding products which are paler in colour than gold, and possess a greenish tint if the zinc be in considerable proportions; but the alloys are

more or less brittle, and have a specific gravity above the mean of their constituents.

Gold with copper and zinc constitutes an alloy used for pencils, chains, etc., the zinc, however, rendering the gold paler in colour, besides inducing brittleness in the alloy.

Platinum frequently occurs in small quantities in commercial gold, especially that derived from Russia; since the ordinary refining operations, as applied to gold, do not effect the elimination of this metal; it does not, however, impair the malleability of the gold.

Palladium, like platinum, is only separated from the gold with which it occurs with considerable difficulty; and hence it occasionally occurs in gold derived from Brazil, etc., and but small proportions of this metal render the gold brittle.

The gold from California is frequently contaminated with traces of an *osmium iridium* alloy; probably not, however, truly alloyed with the gold, but only dispersed in scales or grains throughout its mass, rendering the gold brittle and hard in the coining-press.

141. Occurrence of Gold.—Gold occurs very widely distributed in nature, and almost always, but not invariably, in the *native state*; the native metal being found in the crystalline, metamorphic, and trachytic rocks, as in veins or lodes of quartz traversing slaty deposits, and less abundantly in granite rocks. But by far the most prolific deposits hitherto have been the alluvial deposits, resulting from the disintegration by the weathering action of the atmosphere and running waters upon the ancient gold-bearing strata, constituting the sand, gravels, clay, and detritus known as *drift-beds* or "streams," which have been carried down and deposited by rivers flowing from the mountainous regions of the primitive rocks; in the latter case the metal being most abundantly accumulated at the bends in the beds of such streams.

Native gold occurs invariably associated with more or less of silver, while copper and iron are also frequently present in small proportions; and the native metal from particular sources is also remarkable from the presence of small quantities of other rarer metals. Thus, a telluric gold occurs in Hungary and Transylvania; platinum is frequently associated in small quantities with gold from the Urals; traces of

palladium occur in Brazilian gold, and so on. But some of the purest specimens of native gold, containing 99 per cent. of the latter, have been derived from the Ural district, while other specimens of the native metal from other sources will not contain more than 60 per cent. of gold, the residue consisting chiefly of silver, with variable proportions of copper and iron. Native gold occurs in filiform, granular, reticulated, arborescent, and occasionally in crystalline forms, also in thin laminæ and flattened grains traversing or distributed through the quartz or other auriferous rock, its dissemination frequently being so fine that a rock presenting to the eye no evidence of the presence of gold, will yet prove highly productive of the metal; while in gravel and sand detritus the metal occurs in rounded or nodular masses more or less mixed with quartz, and also in the form of very fine grains or dust; the masses when of any considerable size being designated as "*nuggets*," such occasionally occurring of from a few pounds to as much as 2 cwts. in weight; and the metal is sometimes also found crystallised in forms of the regular system. Veins of iron and copper pyrites, galena, argentic sulphide, etc., traversing crystalline rocks are frequently sufficiently auriferous to permit of the profitable extraction of the gold, although the latter may be present in insufficient quantity to render it visible before smelting.

Native gold occurs in almost all parts of the globe. In Europe the mines of Hungary and Transylvania yield the largest proportion; though Piedmont, Spain, Switzerland, France, Silesia, Sweden, the sands of the Rhine and Aar yield small portions of the metal, but they are mostly non-remunerative sources. It occurs occasionally in the rivers and streams of Cornwall, in North Wales, Ireland in the vicinity of Wicklow, and in the Lead-hills of Scotland. Asia supplies numerous gold-producing districts, chiefly in the Urals and Siberia, where its mining is conducted both in deep mines of the quartz rock itself, as also in alluvial deposits; and gold is also found in China, Japan, Hindostan, and the East India Isles. Africa again furnishes gold chiefly in the form of dust obtained by the washing of alluvial deposits, the sands on the coast of Caffraria opposite Madagascar being reputed to be of great richness. Gold dust also

occurs south of the Great Sahara between the river Senegal and Cape Palmas. In South America the chief gold-mining districts are in Brazil, New Granada, Venezuela, Peru, and Chili; and the gold-bearing districts of North America are Mexico, the Southern United States (viz., Virginia, North and South Carolina, and Georgia), British Columbia, Nova Scotia, but most abundantly in the more modern gold-mining district of California, where the gold occurs chiefly in the alluvial deposits of quartz and granite detritus deposited by the Sacramento and other rivers, and is largely alloyed with silver. Australia has furnished and continues to yield very large quantities of gold, the gold-mining districts being chiefly westward of Bathurst and in the Victoria Colony; here it occurs associated with quartz, and though formerly most of the gold was obtained by surface work, at the present time deep quartz mining is extensively carried on, yet *gold dust* and *nuggets* continue to be found in alluvial deposits, formed by the crumbling down of the rocks under atmospheric influences. Gold is extensively obtained from New Zealand and Van Diemen's Land, where it is derived chiefly from alluvial soils and river workings, although quartz mining is also carried on.

Nagyagite is a native telluride of gold and lead, which occurs associated with auriferous blende, manganous silicate, and sometimes antimony ores, at Nagyag and Ofienbanya in Transylvania, as also in Virginia. This mineral is a soft opaque mineral, black or lead-grey in colour, and possessing a metallic lustre, occurring sometimes lamellar, at other times granular. It melts easily before the blowpipe, leaving a button of metallic gold. Nagyagite contains about 30 per cent. of tellurium, 50 per cent. of lead, with from 6 to 10 per cent. of gold, along with sulphur, and small proportions of silver, copper, and sometimes antimony.

142. Gold Mining.—Formerly almost the whole of the gold was extracted from stream works or surface workings, and the operations used for its separation were largely of the mechanical nature required for the separation of earthy matters, clay, sand, etc., with which the metal was mechanically mixed; but in more recent operations the work has assumed a more systematic mining character, and the amount

of gold obtained by quartz mining now exceeds that produced from the alluvial workings. The quartz rock itself, containing the gold in minute particles, and generally mingled with pyrites, zinc blende, and other minerals, being worked to considerable depths; for which purpose the quartz is crushed, stamped, etc., and the gold subsequently extracted by washing operations suitably conducted, by amalgamation, or by treatment by one of the other processes to be mentioned for the extraction of the gold; while any copper the gold contains is separated by *cupellation*, and the silver by a process of *parting*.

In surface workings for the extraction of gold from alluvial deposits, sands of rivers, etc., the *gold diggers* or *gold washers* first commence operations by "*prospecting*" the soil, in which operation specimens of the ground are introduced into a shallow basin or bowl of about 12 inches in diameter, in which the material or dirt is washed with water after the manner subsequently carried out on the large scale, and by which the lighter earthy portions of the soil are carried away, leaving in the pan any metallic residue which was contained in the specimen under trial; and from this preliminary *assay* it is determined whether the soil of the locality is sufficiently auriferous for profitable working. It may be necessary to remove or excavate a certain depth of soil, peat, sand, or gravel from the surface before attaining to the auriferous alluvium, such a covering in the Russian stream works of the Ural Mountains attaining to a thickness of 70 feet before the drift-deposit or "*pay-dirt*" containing the gold is attained, but such is the greatest thickness of cover yet met with; while in other localities the gold will occur almost upon the surface of the ground.

The locality having been thus approved by prospecting, the operations are continued, the diggers working independently, or more usually in gangs of about four men each; and the washing of the soil is conducted either in the zinc or iron pan just mentioned, and which is chiefly used in South America; or long shallow troughs are employed, the bottoms of which are lined with a material as baize, blanket, or tanned skins retaining the hair, which coverings serve to further resist the tendency of the water to carry away the finer particles of the gold along the bottom of the trough; or

as yet more extensively employed in the diggings of Australia and California, is the "cradle" or "rocker," of about 7 feet in length and 2 feet in width, the top end being raised about 4 inches higher than the foot, while the foot is perforated with a number of holes for the escape of water and fine earthy matters, and at the upper or head-end of the cradle is placed a sieve which separates the larger stones, which are then removed by hand. The current of water poured by one of the men on to the materials in the sieve, carries the finer and lighter particles through and along the bottom of the cradle, so that the heavier metallic portions collect in the bottom of the trough, the progress of the heavier portions along the length of the trough being still further impeded by a number of cross-ribs or riffle-bars placed on the bottom, and the man keeps the whole in a constant state of agitation or motion upon the rockers of the cradle. In this manner the heavy metallic particles, with small quantities of earthy matters, are collected on the bottom in front of each cross-bar or rib of the cradle bottom, and the material so obtained is then dried in the sun. The lighter earthy particles, black sand, etc., still associated with the metal are blown away by bellows, and the metal is then ready for fusion; but if the gangue of the materials operated upon contain much stiff clay, then it is first subjected to disintegration before washing upon the cradle, the disintegration being effected by placing the materials in a suitable vessel or tub, and thoroughly agitating it with water, either by means of spades or revolving arms.

The operation of "*washing in the pan*," already noted, is conducted by first filling the pan about three-fourths full of the auriferous dirt, when the pan is placed beneath the surface of water, and held in a somewhat inclined position, so that, by shaking and agitating the contents of the pan in this position, the clayey and lighter particles are continually washed over the edge of the pan, the miner resting the pan upon the bottom at intervals, so as to break up with his fingers any portions which may be imperfectly wetted. There is, in this manner, left in the pan only the particles of gold, together with a quantity of black sand, etc., which is removed as before by drying, and then blowing away by a gentle blast of air.

The apparatus known as the "*sluice*" has most generally superseded the older forms of cradle and tom in all extensive workings of pay-drift. This apparatus consists of a long wooden trough, or rather series of smaller troughs of some 10 or 12 feet in length, and made somewhat taper, so that the smaller end of one enters and fits into the wider end of the next, and so on, the whole constituting a trough of several hundred feet in length, and varying from 1 foot 6 inches to as much as 6 feet in width. This trough is generally supported upon trestles at a variable height above the ground, and so that it is inclined at the rate of from 1 inch to $1\frac{1}{2}$ inches in the foot. Along the bottom of the sluice are placed a number of bars, or as they are called, "*riffles*," arranged, according to circumstances, either lengthwise, crosswise, at an angle, or so as to direct the water in a zig-zag course along the sluice, whereby the heavier particles of the ground materials are collected in front of these bars; while in other localities a series of rectangular recesses are formed in the bottom of the sluice for the purpose of collecting the gold, amalgam, and mercury. The drift is thrown in by shovels at the head of the sluice, through which a current of water is maintained, whereby, as in the previously described apparatus, the finer and lighter particles of earthy matters are carried to a greater distance along the sluice; while the riffle bars also serve further to check the onward course of metallic particles. Mercury is supplied near the head of the sluice, or at some distance below, according to the condition in which the gold exists in the drift; if wholly as fine particles, the mercury is allowed to drop slowly on to the sluice at its head; while, if a portion exist as coarser particles, which separate near the head, then the mercury is introduced lower down, so as to amalgamate with and collect the fine particles collected on the bottom and along the edges of the riffles, etc.; while it is a frequent device adopted for the collection of the very fine dust escaping with the water from the foot of the sluice, to introduce at this point an amalgamated copper plate (that is, a copper plate whose surface is amalgamated with mercury, by applying the latter to the clean surface of the former); such a plate collecting upon itself (mercury being added at intervals) the finer particles of gold, while its surface is preserved from

the wear and scratching that would be produced by sand and pebbles passing over it by the introduction of a riddle above the plate, which thus prevents the passage of the heavier particles over the plate; and in this manner there escapes from the last trough of the series only a slime or mud practically free from gold.

The separation and collection of the gold amalgam and mercury, from the sand and gravel collected upon the bottom of the sluice, is effected at intervals of eight or ten days; for which purpose, having ceased to throw in the drift, a number of the riffle-bars near the head of the sluice are removed, and the metal, amalgam, and sand collected between them is then further washed for the better separation of the non-metallic portions; while the heavier metallic portions collect between the lower riffle-bars, from which it is then scooped out. A series of riffle-bars lower down is then treated in a like manner, and so on until the whole are removed, and the gold, amalgam, and mercury collected, the whole operation being known as "*cleaning up.*"

The amalgam thus obtained is pressed through canvas bags for the separation of the excess of mercury, after which the mercury is distilled off from the auriferous amalgam so obtained.

The above methods of washing apply chiefly to the separation of gold dust from surface alluviums and sands; but if the *auriferous rock* or *gold quartz* be the subject of operation, it requires to be extracted from the mineral vein in the manner of ordinary mining operations, and afterwards to be crushed or stamped and ground to powder preparatory to its metallurgical treatment proper. The *crushing* of the ore is effected in a variety of ways; but a useful machine consists of a pair of rollers of cast-iron kept in contact by a weighted lever, which thus applies the necessary pressure to the rollers to enable them to break up the bulk of the ore, and is yet sufficiently elastic to permit of the separation of the rollers for the passage of specially hard pieces without interfering with its general working; while the ground ore from the rollers is received into the top of an inclined, perforated, and revolving cylinder, so that, as the ore moves towards the lower end, the finer particles pass through the meshes on to

the floor, while the coarser portions are accumulated at the bottom end of the cylinder.

Stamping of the ore reduces it to a finer state of division than is accomplished in the crushing rolls; and is the method now most generally employed for the treatment of auriferous quartz. The operation is conducted in a stamping-mill, consisting of a range of large vertical wooden beams or pestles shod with iron, and weighing from 5 to 8 cwts. each. About five of these are arranged in one machine, and are worked either by a cam actuated by animal, steam, or water power; by an endless chain, or by any other contrivance for raising the pestles vertically, and then allowing them to fall in regular sequence upon the ore contained in a trough resting upon a hard foundation of iron or of beaten stone; while a current of water passes through the mill and carries the powdered ore on to a sluice, similar to that already described. If the ore or gold-bearing rock requires to be reduced to a finer powder than is effected by the stamps, it is then subjected to the operation of *grinding* in a mill or arrastra, consisting of iron or granite edge stones driven by animal or other power, beneath which the powdered ore is ground, and where also the washing of the ore and its amalgamation are sometimes commenced. The quartz rock thus reduced to a fine powder, is usually subjected to a more or less carefully conducted *washing* for the separation of the lighter non-auriferous portions, so as to reduce the quantity of materials to be operated upon in the amalgamation process.

The *washing* operations are conducted upon various arrangements of a series of slightly inclined troughs, along which a gentle stream of water is maintained, as in the method of "*sluice-washing*" above described. In another arrangement the washing is conducted upon *cloth-covered tables*, or upon *blankets* stretched upon frames, the mode of operation being the same as in the last case, except that the workman facilitates the removal of the earthy matters by agitating the materials by means of brooms of heather, or by a kind of hoe moved gently in a direction opposed to the current of water. The largest proportion of the gold or auriferous schlich thus collects upon the first blanket; and after certain intervals these blankets are removed, and washed in tanks to

free them from the grey or black auriferous schlich with which they have become covered; after which the blanket is again ready for a repetition of the process. Or, instead of removing the blankets or cloth-covered tables, in Transylvania, etc., two or more traps are placed in the length of the washing apparatus, into which the different qualities of schlich collected upon the woollen coverings are swept or raked at intervals, and in these undergo a further separation by subsidence. In a further arrangement used in the Ural districts, etc., the water is pumped into a tank at the head of the washing tables, from which it is delivered into the two ends of a revolving, conical, and perforated cylinder of sheet-iron, placed on a horizontal axis above the head of the tables. Into the smaller end of this cylinder is also delivered the auriferous powder; and, as the cylinder revolves, the materials will thus pass from the smaller to the wider end; the water and finer particles at the same time passing through the perforated cylinder on to the washing table beneath, where the fine particles collect as in the previous arrangement, while the water or schlich, escaping from the end of the table before finally running away, is passed through tyes or tanks at the foot of these tables, and in which the schlich is thoroughly agitated for the further separation by subsidence of any small proportion of metallic matters which it might still retain; while the pieces of gold or quartz which are too large to pass through the meshes of the cylinder, pass out at its wide end on to a table, where the particles of gold, after rubbing against each other in their passage through the cylinder, have become burnished and are readily discernible; when such pieces are then picked out from the larger pieces of unproductive quartz.

PROCESSES FOR THE EXTRACTION OF GOLD.

The operations hitherto described of separating the gold from the sand, clay, or quartz with which it occurs mechanically mixed, serve only to prepare the mineral for its metallurgical treatment proper; for whether the metal be obtained as *gold dust* from surface workings, or from the quartz rock, it still requires a further treatment for its concentration and purification; for which purposes several methods are pursued,

amongst which may be noted— 1° , the *amalgamation method* for the treatment of auriferous quartz, pyrites, etc.; 2° , the methods of extraction by direct *smelting operations*, with the use of lead as a means of collecting and concentrating the gold from auriferous quartz and pyrites; 3° , the proposed methods of *Longmaid* and *Anossow*, in which *iron* is employed as a medium for the separation of the gold from gold quartz or sands in the smelting of the latter; 4° , *Plattner's process* of extraction by treatment with chlorine; and 5° , the *melting of gold dust*. The particular method adopted is largely influenced by the nature and amount of the foreign matters with which the gold ore delivered to the metallurgist is still associated; and of the foreign matters thus occurring in auriferous minerals may be noted: *silica*, as quartz or common sand; *earthy matters*, as clay, magnetic and other oxides of iron; *iron pyrites*, *galena* (PbS), *blende* (ZnS), one or more of which is usually retained in mechanical mixture by the metal prior to its fusion; while certain complicated ores, as those of South America, besides containing almost the whole of these, are frequently contaminated with arsenic and antimony in addition.

143. Amalgamation of Auriferous Quartz.—The method of amalgamation is especially applicable to the treatment of auriferous quartz, or other ores in which the gold is disseminated throughout the gangue in an exceedingly fine state of division, and in which it is therefore difficult to separate and collect the whole of the gold by washing operations alone; and for the latter reason amalgamation is also frequently applied to the treatment of auriferous sands and soils, after they have been concentrated to a certain extent by washing, and the larger portions and grains of the metal have thus been separated, when, as the metal can be more completely extracted by amalgamation than by any method of washing, the concentrated material is then treated with mercury. In the treatment of *gold quartz* or other hard ores it is not unusual to *roast* them prior to amalgamation, by which sulphides and arsenides are converted into the lighter oxides, which are then readily washed away; while the rock is at the same time rendered much more friable and easy to break up under the stamps.

The amalgamation of the ore, ground in the manner already described, is effected in amalgamating mills of various constructions, but all possessing a certain amount of grinding action upon the charge of mercury and auriferous materials to be acted upon, with the necessary speed to stir well, or keep the charge well agitated. Such a mill employed in Piedmont, where the ore is chiefly an auriferous pyrites, is represented in vertical section by fig. 66, and consists of a series of amalgamating machines arranged in tiers; so that the charge, as it overflows the first, is delivered into the second, and so on to the third and fourth, each machine being like its predecessor, except that the table upon which it is supported is lower than the one preceding it in the series, in order to admit of the flow of the charge from the higher to the lower, as already mentioned. Each machine consists of a cast-iron dish α , bolted to the top of its table, and through the bottom of which passes the vertical shaft carrying a spur-wheel, which gears with a similar wheel on the next machine in the series; while on the top of the vertical shaft or axis is supported a cross-head, from which is suspended, by a pair of iron rods, the large muller e, e , of hard wood, and furnished with a number of iron ribs on its under surface, which come almost into contact with the inner surface of the cast-iron dish α ; while the body of the muller leaves a space of about half

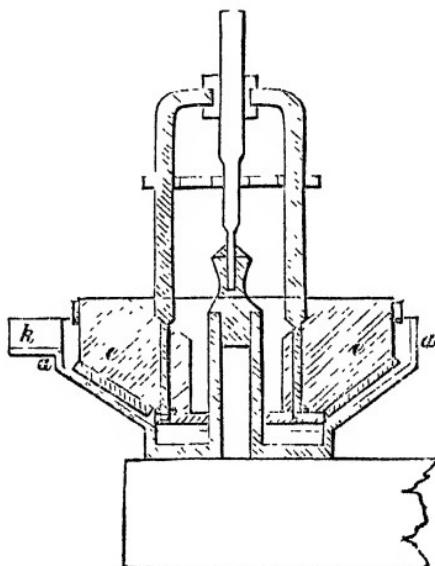


Fig. 66.—VERTICAL SECTION OF THE MILL FOR AMALGAMATING AURIFEROUS PYRITES.

from which is suspended, by a pair of iron rods, the large muller e, e , of hard wood, and furnished with a number of iron ribs on its under surface, which come almost into contact with the inner surface of the cast-iron dish α ; while the body of the muller leaves a space of about half

an inch between it and the surface of the dish. The upper surface of the muller is hollowed out as shown, forming a kind of funnel for charging the machine. About half a hundredweight of mercury, forming a depth of about half an inch on the bottom of the dish *a*, is first introduced into each machine, which is then set in motion at the rate of some twenty revolutions per minute; and the ground ore is delivered from a spout by a stream of water passing through the grinding apparatus into the cavity of the muller, from which it passes out at its centre or apex, into the space between the muller and the outer cast-iron pan in which is contained the mercury; and where, by the rotation of the muller with the iron ribs on its lower face, the materials are thoroughly incorporated and passed gradually towards the periphery of the machine, the fine particles of gold being rapidly attacked and dissolved by the mercury; while, as the first machine overflows by the continual introduction of fresh materials, the charge flows out by the spout *k*, and is delivered into the concavity of the muller of the second apparatus, and so on to the end of the series, whereby the particles of gold escaping amalgamation in the first machine are thus arrested in the second, third, or fourth vessel. The working is continued for a variable time, according to the richness of the materials operated upon, recharging with mercury only taking place when that already introduced begins to lose its liquidity, which it does when it has taken up about one-third of its weight of gold; and it is further necessary that the rotation be not continued too long, otherwise a loss of mercury arises from *flouring*, and probably also from the formation of a sulphide of mercury, which is then washed away by the stream of water from the heavier amalgam left in the machine. When the amalgamation is thus judged to be completed, the amalgam is drawn off, washed, and strained through leather bags, by which any excess of mercury passes out, and there remains a semi-solid amalgam containing about 35 per cent. of gold, which is moulded into balls, and from which the mercury is separated by distillation in an iron retort, with the condensation of the mercury in water. The metal thus separated is afterwards fused in black lead crucibles beneath a layer of borax, and then cast into ingots by pouring it into open cast-iron moulds.

Attwood's machine, as used in California,* for amalgamating the washed auriferous ore, consists of an inclined plane, at the head of which is a trough in which works a pair of wooden rollers, upon the circumference of which is fixed a number of slips of iron. Thus when the rollers are set in motion by band and pulley connections, the ore delivered into the trough from a hopper placed above, along with a stream of warm water admitted at the same time, are thoroughly incorporated with the mercury contained in the trough, and in which the gold is dissolved; the mixture of amalgam, mercury, and other materials then passes from the trough over the inclined plane, the latter being divided into channels, and provided with amalgamated copper plates for the collection of the auriferous amalgam, whilst any excess of mercury flows off and may be again used.

In the Alps, etc., the amalgamation is effected by delivering the ground ore from a hopper into a horizontal hollow cylinder, in which a millstone revolves, and where the ore is mixed with water into a kind of slime, a quantity of common salt (NaCl) being also sometimes added. This slime is then washed by a current of water into three iron cylinders, in which the amalgamating mills revolve, and here the auriferous slimes are thoroughly agitated with the mercury, whereby the gold is dissolved; after which the mixture from the mills is subjected as before to a further washing for the separation of amalgam, mercury, and gangue.

As in the methods described for the amalgamation of silver, it is necessary to properly proportion the quantities of ore, water, and mercury operated upon in the amalgamation process, otherwise an unnecessary loss of mercury and gold is entailed. Owing to an alteration of the surface of the gold from various causes, as from the presence of arsenic, sulphur, etc., in the ore, it is sometimes difficult to make the mercury adhere to, or wet its surface, and the metal thus escapes amalgamation; and to overcome this difficulty, it has been proposed to add to the mercury about 1 per cent. of an amalgam of mercury containing from 3 to 4 per cent. of sodium, instead of using mercury alone, under which circumstances the surface of the gold is readily attacked under

* Phillips' *Metallurgy of Gold and Silver*.

all conditions; while Crookes also proposes to add to the sodium amalgam a proportion of zinc, or of zinc and tin, in addition.

The amalgam obtained from the amalgamating apparatus, of whatever form, is separated by washing and pressure from any excess of mercury, and the semi-solid amalgam remaining is then pressed into masses, which are introduced into iron retorts for the separation of the mercury from the amalgam. The necks of the retorts are connected with pipes leading to a vessel of water, in which the mercury is condensed and collected as the temperature of the retort is gradually raised to the degree required for the distillation of mercury; care being taken not to raise the temperature too quickly nor yet too high, otherwise the porous, spongy, metallic mass remaining in the retorts at the conclusion of the distillation, is apt to retain portions of mercury, as also to adhere to the sides of the retort. The spongy metal thus obtained still contains silver, and perhaps copper or other non-volatile alloys extracted from the quartz, which it is necessary to remove in the subsequent fusion of the metal.

144. Smelting of Auriferous Quartz.—Numerous methods have been proposed for the extraction of gold from auriferous quartz and pyrites, by smelting operations; but it is obvious from the small proportion of metal present in the quartz, that simple heating in a furnace will not suffice to collect the metal from the mass of *infusible* quartz. Accordingly, advantage is taken of the affinity, at high temperatures, of lead for gold; and this metal, its sulphide (galena), oxide (*litharge*), lead slags, or other material, which mixed with carbonaceous matters, scrap iron, or other suitable reducing agents, is capable of yielding metallic lead in the furnace, is added to the furnace charges, thereby increasing the amount of metallic matter in the charge, and at the same time of collecting the finely disseminated gold; the lead thus discharging, at the high temperature of the furnace, the same function which mercury performs at ordinary temperatures in the amalgamating process. Further, to allow of the more ready separation of the gold, it is necessary to add a material as lime, lime and clay, fluor-spar, or oxide of iron, which at a sufficiently high temperature combines with the quartz or silica, with the

formation of a fusible slag or flux, from which the gold, or alloy of gold and lead, with any silver that may be present in the ore, readily separates and collects in the hearth of the furnace beneath the fused slag. The alloy so collected is then to be cupelled for the separation of its lead, copper, etc., in the cupellation furnace, exactly in the same manner as described when treating of the cupellation of silver (p. 274), except that, instead of a cake of silver remaining, the product is essentially an alloy of gold with variable proportions of silver, from which alloy the silver is subsequently separated by one of the methods of "parting," described on page 313.

145. Treatment of Auriferous Pyrites.—The *method of smelting* is also applicable to the treatment of certain poor ores, as auriferous pyrites, in which it is necessary, before treating with lead, to concentrate the gold in a smaller bulk of a ferriferous regulus or matt; and for which purpose the ore is first imperfectly roasted or calcined, an operation that may be effected in a special furnace, or in heaps in the open air; the ignition of the sulphur in the ore being effected by placing the latter upon a layer of brushwood or other fuel, when the combustion is continued to the desired extent by the oxidation of the sulphur in the ore, and thus the iron is partially converted into oxide, with the elimination of a certain amount of sulphur. But since the object in the subsequent fusion is to obtain a regulus or matt, it is necessary that this roasting be not carried too far, but that sufficient sulphur be left in the ore to combine with the metallic elements, and so produce the desired regulus.

The roasted ore is then treated in the blast furnace, with an admixture of lime, when the quartz (silica), lime, and oxide of iron combine, with the production of a fusible slag or flux, beneath which collects a regulus or matt of ferrous sulphide, containing also the gold, silver, etc., of the ore. This auriferous regulus is then the subject of a further concentration, by a repetition of the partial roasting and subsequent fusion as before; or the regulus is mixed with a fresh portion of calcined ore, along with a little lime, and the fusion repeated, by which a further proportion of gold is thus added to the first regulus. These operations of alternate calcination and fusion are repeated until the regulus is considered to

have acquired the necessary degree of concentration; when the regulus is fused with lead, or a plumbiferous ore, for the collection of the gold, by which an alloy of lead, containing the whole of the gold and silver, collects in the bottom of the furnace, beneath a layer of regulus consisting of ferric sulphide, etc.

The auriferous lead so obtained is then treated as in the previous method, according to the English or German methods of cupellation, and the gold subsequently separated, by the operation known as "*parting*," from the alloy of gold and silver thus obtained.

146. Longmaid's Process.—This is a patented process for separating the gold from quartz or other silicious ores by means of *iron*. For this purpose the ore is finely crushed, then mixed with roasted pyrites or ferric oxide, along with limestone, and sometimes also fluor-spar, the whole being melted upon the hearth of a reverberatory furnace, when a regulus containing the greater portion of the gold, separates beneath the layer of slag or flux, though small proportions of the gold are said to be retained in the flux. Into the melted mass on the hearth of the furnace, plates of wrought iron are introduced, and upon the withdrawal of these they are found to be coated with a film of gold, which is then removed by immersing the red-hot plate into a bath of molten lead, the operation being thus repeated so long as the plates continue to collect any gold from the charge in the furnace. In this manner an auriferous lead is obtained, as in the previous process, and only requires to be *cupelled* for the recovery of the alloy of gold and silver, with subsequent *parting* for the separation of the silver therefrom. This process has not, however, come into extensive use, since, although the gold would entirely collect upon the surface of the iron plates, could contact between the two metals be ensured, yet much gold escapes contact by getting into cracks, etc., of the furnace bed, and so escapes withdrawal by the iron plates.

147. Anossow's Process.—This smelting process, in which iron is again made the medium for collecting the gold, was proposed for the treatment of the auriferous sands of the Ural, but it has not succeeded in being brought into successful application. In this process, the sands were to be smelted

with iron (cast-iron would answer) in a blast furnace, when the gold would be obtained in combination with iron; and for its separation from the latter the alloy was to be treated with sulphuric acid, upon which the iron is dissolved, while the gold is left in the insoluble residue, or the gold might be largely separated from its alloy with iron by remelting with lead, with the subsequent separation of the gold from the lead by the process of cupellation.

148. Plattner's Process.—This process has been applied to the treatment of an arsenical pyrites, worked for its arsenic at the Reichenstein mines in Silesia, and which contains only about 200 grains of gold per ton of ore; as also in California for the treatment of auriferous pyrites. The ore for treatment is roasted in a reverberatory furnace, above which is a condensing chamber, in which the arsenious anhydride (As_2O_3) is condensed and collected as it is volatilised from the furnace charge; while there remains on the hearth a residue of oxide of iron, etc., with a little arsenic, and the whole of the gold; but it is specially desirous to continue the roasting until the sulphur, antimony, and arsenic are expelled as completely as possible, and the iron at the same time converted into ferric oxide. This residue is the subject of the *chlorine process* of Plattner, and for this purpose, after moistening with water, it is exposed in large wooden tubs or other suitable vessels to a current of chlorine gas, which latter should be as free as possible from hydrochloric acid. The chlorine attacks the iron and gold, with the production of their respective chlorides, which, after allowing the charge to remain at rest for from 12 to 15 hours, are then dissolved out by the addition of a definite amount of water; and from this solution, previously made acid by the addition of a little hydrochloric acid, whereby the simultaneous precipitation of the iron is prevented, the gold is then precipitated in Silesia by sulphuretted hydrogen, while a little sulphur from the precipitant will be deposited along with the auric sulphide; but in California the gold is precipitated as a brownish-black deposit by the addition of ferrous sulphate. The precipitate is then collected, washed, dried, and heated in an open porcelain crucible, by which the sulphur is expelled, while the gold is finally extracted by fusion with borax in black-lead crucibles.

In ores free from sulphur, antimony, and arsenic, the gold may be extracted by passing dry chlorine gas over the slightly moistened ore, when, if the operation be carefully conducted, about 97 per cent. of the gold may be thus separated.*

Calvert has also proposed a *chlorine process* for the treatment of auriferous quartz, in which he proposed to subject the finely-powdered ore, mixed with about 1 per cent. of manganese oxide, to the action of a current of chlorine, continued during some twelve hours, after which water was added and allowed to percolate through the mass of ore, draining through the false bottom of the apparatus upon which the chlorinised ore was supported, the same water being, by these means, returned and passed several times over the same amount of ore, so as to thoroughly dissolve out the soluble salts, consisting chiefly of the chlorides of copper, iron, and gold, in the least possible amount of water. The copper is afterwards precipitated from this solution by the addition of metallic iron, and the gold subsequently thrown down in the finely-divided state by means of *ferrous sulphate*.

If the ore contains silver in addition, then Calvert proposed to evolve the chlorine by mixing common salt, black oxide of manganese, and sulphuric acid, with the ore, when the argentic chloride produced under these circumstances is dissolved out in the solution of common salt, the latter being always kept in excess for this purpose. From the solution of mixed chlorides thus obtained, it is necessary to separate the silver, prior to the precipitation of the copper and gold by iron and ferrous sulphate respectively.

149. Melting of Gold Dust, etc.—The gold dust as received from the gold washers, as also the spongy metal left after the distillation of the amalgam obtained in the amalgamation method of extraction, requires careful fusion to separate the gold more thoroughly from smaller quantities of mechanically mixed earthly impurities with which it is still associated; and at the same time, with the exercise of care during the fusion, much of the tin, antimony, lead, etc., that may be present in smaller quantities in the metal, rendering it unfit for direct application to the arts, will be removed, whereby the gold will be left after this melting in such a

* *Chemisches Centralblatt* (1873) page 633.

condition that any further refining operations are unnecessary.

The fusion is effected in thick plumbago crucibles, which require careful annealing before use; and with this object they are first inserted in the furnace with the mouth downwards, the fire being then gradually raised until the pots attain a red heat, when they are removed and reinserted in the furnace in their proper position, or mouth upwards. The charge of gold dust, mixed with a little dried borax, is transferred from a copper scoop to the crucible, and the heat then very gradually raised to the fusing point, upon which a scum or scoriae of the mechanical impurities rises to the surface. This scoriae, also serves to absorb any oxides of lead, bismuth, etc., which sometimes occur in the metal, and, after thickening by the addition of a little bone-ash, the scoria is skinned off and the metal carefully stirred so as to expose it to the air; while if the presence of antimony or tin be suspected in the gold, the addition to the charge of a little nitre is frequently made for their oxidation.

An old practice was to add to the melted metal a small proportion of mercuric chloride, by which a kind of effervescence was set up in the metal, which, it was considered, tended to a more thorough separation of the mechanical impurities; while at the same time eliminating small proportions of such metals as antimony and lead.

The surface of the melted metal having been cleared of the scum, and thoroughly cleansed from fluid oxides, etc., by bone-ash, in the manner above noted, the fluid metal is then cast into bars by pouring it into warmed and greased open iron ingot moulds.

SEPARATION OF GOLD FROM SILVER AND COPPER.

The gold as obtained by any of the methods described in the previous pages, always contains a larger or smaller proportion of *silver* which it is desirable to extract, since, in the sale of the metal, such silver is only reckoned as alloy and paid for as copper; and the gold is, besides, frequently alloyed with small quantities of copper, iron, and other metals. If the gold be required for certain applications in the arts

where these metals would interfere, it becomes necessary to subject the metal to a process of "refining," or, as it is termed, "parting," for the separation of these metals, but notably of silver. The operations of parting are conducted either according to one or other of the "wet methods," where nitric or sulphuric acid constitutes the more general agent employed for effecting the separation; or according to certain "dry methods," in which litharge, sulphur, chlorine, or certain cement powders consisting of common salt and brick dust are employed as the agents, the use of the last-mentioned mixture constituting the cementation method; but these latter methods are of more local and limited application than are the wet methods first mentioned.

"Wet refining," "parting," "quartation or inquartation," are the terms at present or formerly employed to designate the operation by which gold is refined, or separated from silver, and at the same time from any small quantities of copper, antimony, etc., by means of nitric or sulphuric acid; the latter, as being more economical, is preferred where the process is carried on continuously, and where large quantities of metal are to be dealt with; while the former, or nitric acid process, is generally preferred where much antimony, tin, or other readily oxidizable metal is associated with the alloy; as also for the purposes of small assays, though, as a rule, unless special care be exercised, it does not effect the separation of the silver so thoroughly as the sulphuric acid process; whilst the last-mentioned process is so economical, that in France it has been found profitable to extract the gold from old coins which did not contain more than from one to two thousandths of gold, and now silver containing only one-half a thousandth of gold may have the latter profitably extracted by this method.*

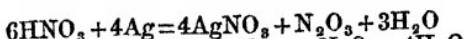
The terms *quartation* or *inquartation*, formerly applied to these processes, have reference to the proportions of silver with which it is necessary to alloy the metal before "parting;" for, previous to the treatment with acids of the gold to be refined, it is necessary to alloy it with about twice its weight of silver, otherwise, on boiling with the acid, the silver would only be dissolved from the surface of the alloy,

* Makin, *Metallurgy*.

the large proportion and density of the gold preventing the action of the acid throughout the mass. Formerly, the required proportions were considered to be 3 parts of silver to 1 of gold, and hence the term "quartation."

150. Wet Methods of Gold Parting.—The first operation in these processes is the making of a preliminary assay, or determination of the relative proportions of gold and silver present in the alloy to be treated, in order that an amount of silver may be added, sufficient to make up the required proportion of two or three parts of silver to one of gold. The metals are then alloyed in the required proportions by fusing them in plumbago crucibles; and after thoroughly incorporating the constituents, the alloy is run or teemed into cold water, by which the metal is obtained in a finely-granulated and flakey condition, readily acted upon by the acid; while, to aid in this granulation, in some cases the crucibles are fitted with lids, through which a fine continuous stream of metal can be delivered into the water. This granulated metal is then treated with nitric or sulphuric acid, according to the method adopted in the parting.

In the "*nitric acid process*" the granulated alloy, prepared as above, is introduced into platinum vessels or digesters; but prior to the introduction of platinum for this purpose, vessels of glass, porcelain, or earthenware were in use; and yet, despite the very considerable first cost of platinum digesters, they are found to be more economical than those previously in use, owing to the considerable loss of gold and silver, etc., entailed by the frequent fracture of the glass or earthenware vessels. The platinum digesters are each placed upon a sand-bath heated by its own fire, and each vessel is likewise fitted with a lid, from which proceeds a long stoneware pipe for the condensation and collection of any acid that may be volatilised or carried over with the large volume of gases (nitrous anhydride N_2O_3 , and nitric oxide N_2O_2) which are evolved during the operation, from the decomposition of the nitric acid by the silver and copper respectively in the alloy, thus—



and which pipe also serves for conveying the non-condensible

gases out into the atmosphere. For each pound of the granulated alloy introduced into the digester, from $1\frac{1}{4}$ to $1\frac{1}{2}$ lb. of nitric acid (specific gravity 1.32) is added, it being necessary that the acid be *free from chlorine* and not too strong; for the presence of traces of chlorine is attended with the solution and loss of a portion of the gold; while if the acid is too highly concentrated, there is a tendency to lose metal by its projection from the digester owing to the violence of the action that is set up. When the charge of metal and acid has been introduced, the joints of the apparatus are carefully luted up, upon which the temperature is very gently and carefully raised, when the action becomes very violent; but towards the end the contents of the digester become more and more tranquil until all action ceases, when the apparatus is cooled and the liquid decanted. A second charge of acid is now introduced upon the residue of gold, with a repetition of the boiling; and when all gases again cease to be evolved, the silver has ceased to be dissolved, and the operation is completed.

The residue of gold left in the digester is then washed, dried, melted, and either run into bars, or granulated as required for weighing out to jewellers; while the decanted liquid consisting of argentic nitrate, with an excess of nitric acid, is either crystallised from its solution and sold for photographic purposes; or the silver may be precipitated as argentic chloride by the addition of hydrochloric acid or of common salt.

If the method of precipitation with hydrochloric acid be employed for the recovery of the silver, and the precipitation is conducted carefully, so as to avoid any excess of hydrochloric acid by leaving a small proportion of argentic nitrate still undecomposed in the solution, the resulting solution of nitric acid ($\text{AgNO}_3 + \text{HCl} = \text{AgCl} + \text{HNO}_3$) may be again used for a repetition of the parting process; while the silver may be extracted from its precipitated chloride by washing the precipitate, then moistening with sulphuric acid, and introducing into the precipitate a number of bars of metallic zinc, by which finely-divided silver is deposited, and zincic chloride passes into solution. When the separation of the silver is complete the zinc is withdrawn, and the finely-divided

silver treated with a little dilute sulphuric acid, to dissolve out any particles of zinc; after which it is washed with water, dried, melted, and cast into bars. Another method employed for the separation of the silver is at once to treat the solution of argentic nitrate with metallic copper, when the metallic silver is at once deposited; while the copper enters into solution as cupric nitrate.

The *method of parting by sulphuric acid* is most extensively and generally adopted on the Continent for the separation of gold and silver upon the large scale, the process being, as already noted, more economical than the nitric acid process, whereby it can be economically applied to the refining of silver containing only .0005 per cent. of gold; but the metal for treatment requires in practice, however, to be alloyed with a somewhat larger proportion of silver than is required in the treatment by nitric acid, and although Pettenkofer has shown that the operation can be conducted by this method when the silver amounts to 1.75 times the amount of the gold, yet, for the ready and perfect separation of the silver, the gold should be alloyed with some four times its weight of silver; whilst the amount of copper in the alloy should be under 10 per cent. of the whole, otherwise an excess of cupric sulphate is produced, which is insoluble in strong sulphuric acid, and accordingly encrusts the granulated metal, preventing contact of the metal with the acid, and so stopping the action. Hence, if the copper exceed this limit, before subjecting the alloy to the parting process it is first granulated and roasted on the hearth of a flat-bottomed reverberatory furnace; after which the cupric oxide so formed is dissolved by treating the roasted product with dilute sulphuric acid, when, if necessary, the operations are repeated until the amount of copper has thus been reduced below the limit of 10 per cent.

The metal having been alloyed with the required proportion of silver by melting the metals in plumbago or wrought iron crucibles, it is then granulated by pouring it into water as in the previous case, and afterwards introduced into the digester with about $2\frac{1}{2}$ times its weight of concentrated sulphuric acid (formerly $3\frac{1}{2}$ parts of acid were used); and it is necessary that the acid be always maintained in excess, in

order to retain the argentic sulphate produced in the process always in solution.

The digesters were formerly vessels resembling stills, each one being set in a frame of wrought iron, and provided with a spout, together with a lid or head, connected by a platinum tube or neck with a long leaden condensing pipe running between two rows of digesters, and which pipe served to convey the liquid condensed products, consisting of sulphuric acid with a little argentic sulphate carried over mechanically, to a reservoir placed for their reception. The condensation pipe is so placed that the particles of argentic sulphate, etc., collecting in it may be washed out into the receiver by a little sulphuric acid; while the gaseous products—sulphurous anhydride—were conveyed forward into a leaden chamber of some 30 feet in length, in which the sulphurous anhydride is reconverted by appropriate methods into sulphuric acid, which is then again used in the process; and finally, before reaching the atmosphere, any gases passing from the condensing chambers are conveyed into a drum containing calcic hydrate.

These platinum digesters are, however, replaced in the larger refineries by vessels of *cast-iron*, white or mottled iron being preferred, it being found that these vessels are unacted upon by the strong acid employed in the operation, since the surface of the vessel becomes coated with a thin layer of metallic silver. Two of these vessels are heated over the same fire, and charges of about 10 cwt. of metal can be heated at once, while about 80 lbs. is the charge of a platinum vessel.

The granulated alloy and the acid having been introduced into the digester, its temperature is then raised to boiling, during which sulphurous anhydride (SO_2) is copiously evolved, with the conversion of the silver and copper into argentic and cupric sulphates respectively, according to the following equations:—



the sulphurous anhydride being conveyed, as already noted, through a condensing apparatus for its collection and utilization. The chemical action continues during from three to

four hours, after which the acid liquid is withdrawn, and a fresh but smaller portion of acid added to the residue in the digester. The boiling is then renewed for a short time, after which the contents of the digester are allowed to remain at rest for some time to allow of the subsidence of the gold; and this forms one of the difficulties of the process; for, during the period of rest, bubbles of gas continue to rise at intervals, raising with them and again diffusing the particles of gold throughout the liquid. When the metal has subsided, the acid liquid is again decanted into vessels lined with lead, where it is considerably diluted, while the gold left in the apparatus requires very careful and continued washing with hot water to free it from argentic and cupric sulphate, the latter being soluble only with difficulty in the acid liquid. After most careful washing, the metal is generally boiled in a *platinum* vessel, for a second short period, along with a further proportion of sulphuric acid, after which the washing is repeated, and the gold is dried, melted, and cast into bars.

The acid liquors containing argentic, and some cupric sulphate, are then treated for the recovery of the silver. The liquid contained in a vessel lined with lead is diluted considerably, and then heated by passing steam from a boiler through perforated leaden pipes into the solution, when the argentic sulphate is dissolved in the boiling water, and the silver precipitated therefrom by the introduction of copper shavings, scrap, etc., the reduction being continued until the solution ceases to give a white muddy precipitate with sodic chloride, upon which the finely-divided grey powder of metallic silver is allowed to subside, and the solution of cupric sulphate is decanted or run off into another vessel. The deposited silver is then collected, well washed, drained, and afterwards pressed by hydraulic pressure for the expulsion of water, when the cakes, after drying, are melted in plumbago crucibles and cast into bars.

The solution containing cupric sulphate is evaporated in leaden pans until crystals form, and in this manner the whole of the copper is extracted as cupric sulphate; after which the excess of acid remaining in the pans, and known as "*black acid*" from its black colour, due to admixture with dust, dirt, etc., mechanically mixed with it, is further concentrated and

either used for manufacturing purposes or utilised in a repetition of the parting process.

The process of *parting* by *sulphuric acid* thus involves the following series of operations:—
1°. Alloying with the proper proportion of silver and granulation of this alloy.
2°. Boiling of the alloy with an excess of sulphuric acid (from two to three times the weight of the alloy) in cast-iron or platinum vessels.
3°. Subsidence of the gold and decantation of the acid solution containing argentic and cupric sulphate.
4°. Further treatment with acid, and decantation of the liquid as before.
5°. After washing the gold, again boiling with sulphuric acid in platinum vessels.
6°. Wash, dry, melt, and cast the gold into ingots or bars.
In addition, there are two subsidiary operations for the extraction of the silver from the decanted acid liquors, viz.:—
1°. Precipitation of the silver by copper plates or turnings introduced into the solution.
2°. To wash well, dry, melt, and cast the deposited silver into bars.

The gold refined by the sulphuric acid process has been found to contain small quantities of plumbic sulphate, and traces of auric sulphide, when lead or auric sulphide has been present in the original gold. Hence, if this method of refining or parting is to be applied, it is necessary, if the metal contain lead, tin, or auric sulphide, to remove the sulphur and the first-mentioned metals before treating it with the acid; and for this purpose recourse is usually had to cupellation for the elimination of the lead, while the tin and sulphur are removed by fusion with sodic carbonate and nitre. And in the mints employing the sulphuric acid process, the gold is frequently made a little finer by treating it after parting with sodic sulphate and sulphuric acid, either in iron pans or upon the hearth of a small furnace, by which means a little more silver can usually be extracted, due to the higher temperature that can be attained under these conditions without vapourising the acid.

151. Dry Methods of Gold Parting.—Of the various dry methods employed for the separation of silver, etc., from gold, the “chlorine process,” introduced by Mr. F. B. Miller, has been for some time in use in Australia and New Zealand, for the treatment of gold containing not more than about 10 per cent,

of silver, and from whence favourable reports of its success have been received. It has also been successfully employed for the toughening of brittle gold in the English mint. The chlorine process obviates the expensive necessity of alloying the gold with two or three times its weight of silver, for no other purpose but to ensure success in the process of parting; while for treatment with chlorine the gold is simply melted in a clay crucible, often enclosed for the sake of safety in a second or black-lead crucible. The clay crucible is fitted with a lid, in which is an aperture for the introduction of a clay pipe, by which the chlorine generated in a suitable apparatus is conveyed to the bottom of the melted mass of gold, the surface of the latter being covered with a layer of borax, which thus acts as a cover for preventing the loss of metal by volatilization; while the crucibles are also frequently saturated with a solution of the same salt, so as to render them non-absorbent or impermeable to the fused argentic chloride produced in the process, and which it is one object to collect for the extraction of its silver. The chlorine thus conveyed beneath the molten gold is for a period absorbed as quickly as it is introduced, attended with the conversion of the metals—arsenic, antimony, bismuth, lead, and zinc, which may be associated with the gold—into their respective chlorides, which are volatilised at the temperature employed; whilst the silver collects in a fused state as argentic chloride.

The first stage is marked by the escape of white vapours, consisting chiefly of the chlorides of the baser metals; but after a time orange-coloured vapours begin to appear above the metal, indicating that the process is completed, after which, if the current of chlorine be continued longer, a portion of the gold will be attacked and give rise to a small loss, although auric chloride is again decomposed at a temperature of about 420° F. (216°C.). Accordingly, on the appearance of coloured vapours, the crucible is withdrawn from the fire and allowed to rest for a period of about 10 minutes, or until the fused gold has set, when the still fluid argentic chloride is poured out into a flat mould, forming a slab of a convenient form for its subsequent reduction, and separation of the small proportion of gold which it still frequently retains. The refined gold is now remelted and cast into bars in the usual manner.

The slab of argentic chloride is either at once treated for its silver by placing it between a pair of wrought-iron plates, and immersing the whole for about twenty-four hours into a dilute solution of sulphuric acid, by which treatment the silver is wholly reduced; or, since the argentic chloride obtained as above frequently retains small quantities of gold, Miller proposes to first fuse the chloride with a little potassic carbonate, by which a small quantity of the silver is reduced, which, in separating from the mass and collecting in the bottom, takes up and alloys with the whole of the gold. After this treatment the silver is reduced from the argentic chloride in the manner indicated, while the gold originally contained in it has been thus concentrated in a small button of metal.

The method of separating gold and silver by means of *litharge* and *sulphur*, sometimes employed in the treatment of alloys poor in gold, is, however, only a method for the concentration of the gold in a smaller quantity of silver, which alloy then requires treatment by one of the "wet methods" for the separation of the two metals. For concentration according to this method, the granulated alloy is fused with three-tenths of its weight of sulphur, and a little litharge is then added. In this manner sulphurous anhydride is evolved, and a regulus of plumbic sulphide, containing also silver, separates and floats above a metallic product consisting of a portion of the silver with almost the whole of the gold; and, on cooling, the metallic portion is readily detached from the reguline mass above, by simply breaking up the mass. Thus, by repeating the treatment upon the concentrated alloy of silver and gold so obtained, a further increase in the proportion of gold present in the metallic portion may be effected, and the operation is thus repeated until the gold constitutes about one-fourth of the alloy, from which the gold is finally separated by either the sulphuric or nitric acid process of parting; whilst the reguline portion first separated upon fusion with litharge, yields a further quantity of silver, which stills retains a small proportion of gold.

Another dry method for the separation of these two metals consists in fusing the auriferous alloy with twice its weight of *antimonic sulphide*, with constant stirring of the crucible charge; while if the proportion of silver exceeds 60 per cent.

of the alloy, then a little sulphur is also added to the charge. By these means an argentic sulphide, retaining a small proportion of gold, is formed, and collects as an upper stratum in the crucible; while the separated *antimony* alloys with the greater portion of the gold, and forms a lower layer in the crucible. The fusion is repeated upon the argentic sulphide, with the addition of a further proportion of antimonic sulphide, by which a further quantity of gold is collected as before, as an alloy of antimony and gold. The gold is then separated from this alloy by the oxidation of the antimony, effected either by treating the alloy in a muffle, by fusing the alloy and oxidizing the antimony by directing a blast of atmospheric air upon it, or the oxidation is effected by fusing the alloy with three times its weight of nitre.

A dry method known as the "cementation" plan is adopted in America, according to which process the granulated alloy is interstratified in crucibles or pots of porous clay, with a "cement powder" consisting of 1 part of common salt (NaCl) with 2 of brick-dust (burnt clay). The pots thus charged contain from 10 to 15 lbs. of the alloy with the necessary amount of cement powder, when they are covered with lids and introduced into wood fires, where they are heated to redness, and the heat maintained for from 24 to 36 hours, during which time a large proportion of water is produced by the combustion of the wood, a portion of which obtains access to the contents of the crucibles through their porous walls. In this manner common salt (NaCl), silica, and water, are brought into contact at a red heat, when the sodium of the common salt derives oxygen from the water with the production of soda, which immediately combines with the silica, producing sodic silicate; while at the same time the chlorine from the sodic chloride joins the hydrogen of the water, with the production of hydrochloric acid, and the last mentioned at this temperature attacks the silver with the formation of argentic chloride and the evolution of hydrogen; whilst the argentic chloride is itself fused and absorbed by the brick-dust, leaving thereby a fresh portion of the alloy to be acted upon by a repetition of the same cycle of operations, so that in this manner, by an action of cementation, the gold can be obtained nearly free from silver, or from 21 to 23 carat fine.

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152. Sweep Refining.—Gold sweep is the name applied to the dust of jewellers' and gold or silversmiths' workshops, which is collected and refined by melting it in a reverberatory furnace with a mixture of *coal-slack*, and the finely-ground *lead slags* produced in the ore hearth or other furnace, whereby metallic lead is liberated, and serves to collect the particles of metallic gold contained in the sweep; while to prevent loss of silver in the slag, *scrap-iron* is occasionally introduced, which separates and combines with any sulphur contained in the slag, preventing thereby the escape of the silver, which thus separates in combination with the alloy of gold and lead. These metals are afterwards separated according to the methods already described of cupellation and parting.

CHAPTER VII.

NICKEL.

NICKEL is always associated with, and is very closely allied to cobalt in its chemical qualities and affinities, rendering their separation a matter of some considerable difficulty; and the methods pursued for this purpose are rather chemical than strictly metallurgical processes, since, of the various methods for the preparation of nickel, they all necessitate recourse to a series of wet processes for the final separation of the cobalt, etc., and the production of an oxide of nickel, which processes form an intermediate stage between the concentration of the nickel in a nickeliferous regulus, and the final reduction of the metal by charcoal from its oxide. The price of this metal has much increased of late years, owing to the increased demand arising from its introduction into the fractional currency of Belgium, Switzerland, and Germany; and the increased consumption of its alloys, such as German silver, etc., in the production of numerous articles in imitation of sterling silver, and also as a medium for the reception of electro-plate. This metal, alloyed with iron, forms a principal ingredient of those remarkable bodies known as *meteoric stones* or *aerolites*.

153. **Physical and Chemical Qualities.**—Nickel is grey, approaching almost to a silver whiteness in colour; it is *ductile*, *malleable*, *weldable*, and *very tenacious*, in which latter quality it rivals iron. But its malleability is impaired by the presence of copper, while the same metal increases its fusibility, pure nickel requiring a very high temperature for its fusion, though it is somewhat more fusible than wrought iron; while nickel containing small quantities of carbon is more fusible than the pure metal. The presence of a little cobalt is said to increase the ductility of the metal.

Nickel in the massive state does not readily tarnish by exposure to the atmosphere; but in the finely-pulverulent state, as obtained by the reduction of its oxide by hydrogen, it is spontaneously inflammable, and if heated and then immersed in oxygen, it burns like iron, with the production of oxide of nickel. This metal is magnetic at ordinary temperatures, but loses its magnetism by heating to 250° C. (482° F.), again recovering the quality upon cooling. Its specific gravity ranges from 8·6 to 8·8 according to the mechanical treatment it has received. At high temperatures it is reduced from its oxide by carbon, carbonic oxide, or hydrogen; and it is soluble in nitric or nitro-hydrochloric acid, the solutions of its salts having a green colour. With arsenic it forms an important natural and artificial product known as "*speise*." Nickel is of somewhat extensive application for the manufacture of white malleable alloys with copper, zinc, etc., constituting *nickel* or *German silver*, etc. The chemical symbol of nickel is Ni, and its atomic weight is 58·8.

Commercial nickel is rarely pure, but often contains only from 56 to 86 per cent. of nickel, as indicated by the following analyses of Lassaigne—

ANALYSES OF COMMERCIAL NICKEL.

	German Nickel.	English Nickel.
Nickel,	56·75	73·30
Cobalt,	22·10
Copper,	27·50	trace
Iron,	12·05	1·0
Arsenic,
Alumina,	2·50
Silicious residue,	3·70	·50
	100·00	99·40

154. Nickel and Oxygen.—Nickel combines in two proportions with oxygen, yielding thereby a protoxide or nickelous oxide (NiO), and a sesquioxide or nickellic oxide (Ni_2O_3).

Nickelous oxide (NiO) is an olive or greyish-green powder,

produced by igniting nickelous nitrate or carbonate in closed crucibles. It is non-magnetic, does not absorb oxygen from the atmosphere, and it constitutes the base of the salts of nickel. It is reduced by hydrogen at a red heat, and by charcoal at a white heat, the latter decomposition forming one of the stages employed in the preparation of metallic nickel; according to which a nickelous oxide is first separated, and this is heated with charcoal in clay cylinders for the reduction of the metal.

The hydrate of this oxide is precipitated as a pale apple-green precipitate, when caustic potash is added to a solution of a soluble salt of nickel. Nickelous hydrate is soluble in acids and also in ammonia; and on the application of heat it parts with water and yields, if the temperature be not too high, the higher or nickelic oxide.

Nickelic oxide (Ni_2O_3) is obtained upon the calcination of nickelous nitrate or carbonate at a red heat, when it forms a black powder, which, at a higher temperature, is resolved into nickelous oxide and oxygen.

155. Nickel and Sulphur.—Nickel unites with sulphur in three proportions, yielding thereby a di-nickelous sulphide (Ni_2S), a protosulphide or nickelous sulphide (NiS), and nickelic disulphide (NiS_2).

Di-nickelous sulphide (Ni_2S) forms a pale yellow, brittle, magnetic, and readily fusible body, produced when the sulphate of nickel is reduced in a current of hydrogen gas.

The *protosulphide of nickel* or *nickelous sulphide* (NiS) constitutes the most important combination of these elements, occurring native as nickel pyrites or capillary pyrites described under the ores of nickel. It also results when sulphur is fused with finely-divided nickel, likewise when sulphur acts upon oxides of nickel heated to redness, or when nickelous oxide is ignited and reduced by a current of sulphuretted hydrogen. An impure variety also results upon the reduction of nickelous sulphate by carbon. The direct union of nickel and sulphur is attended with the production of light, the combination taking place with considerable violence, and at a temperature below the melting point of sulphur. This sulphide is a brass-yellow body, with a metallic lustre; it is decomposed by ignition in air or when heated in chlorine

gas, but not by hydrogen at a red heat; and it is not so readily fusible as the sulphide first described.

A *hydrated* nickelous sulphide is precipitated as a dark brown or black precipitate upon the addition of ammonic sulphide to a neutral solution of any salt of nickel; but it oxidizes by exposure to the atmosphere, with the production of a soluble sulphate, and it is also sparingly soluble in an excess of ammonic sulphide. If heated out of contact with the air the hydrated sulphide parts with its water and yields the anhydrous sulphide.

Nickelic disulphide (NiS_2) forms a steel-grey powder when a mixture of nickelous carbonate, potassic carbonate, and sulphur is heated to dull redness. It is decomposed by chlorine with the production of the chlorides of nickel and sulphur.

156. Nickel and Arsenic.—A combination of these elements occurs native; one of the principal ores of the metal—"copper nickel or kupfernickel"—being an arsenide of nickel, and other ores as *Cloanthite*, *Rammelsbergite*, etc., are essentially arsenides of nickel; while the artificial product known as "*speise*," from which the metal is largely extracted, contains nickel chiefly as arsenide. Union of nickel and arsenic occurs when finely-divided nickel is heated in a closed vessel with an excess of arsenic; and arsenic is made the vehicle for concentrating and separating nickel from most of the other metals (except cobalt), with which it occurs associated, arsenic thus playing a similar part in the metallurgy of nickel and cobalt that sulphur does in copper smelting. Small quantities of arsenic suffice to render nickel readily fusible.

Four compounds of nickel with arsenic, corresponding to the formulae Ni_2As , Ni_3As_2 , NiAs , NiAs_2 , are described as occurring native or as being capable of production artificially, the first-mentioned forming a brittle, non-magnetic body when nickel and arsenic are heated together in the manner stated above, or when arsenate of nickel is heated to whiteness in a crucible lined with charcoal; while the second formula corresponds to a crystallised *speise* sometimes occurring in small works; and the remaining two varieties occur as native products, constituting ores of nickel of more or less importance.

157. Nickel Speise.—This is a brittle, metallic-looking body, consisting essentially of a mixture of the arsenides, sulphides, and occasionally also antimonides of nickel, iron, and copper, which collects in the bottom of the pot in the preparation of *smalts* by the fusion of the roasted arsenides and sulphur-arsenides of these metals with certain fluxes, after the manner detailed on page 342, which product (speise) is then employed as a source of nickel. The composition of this body is indicated by the following analyses—

ANALYSES OF NICKEL SPEISE.

Nickel,	49·5	52·6	36·2
Arsenic,	37·8	34·1	29·9
Cobalt,	3·2	3·3	1·3
Iron,	10·1	1·1
Copper,	1·6	...	1·5
Bismuth,	21·5
Antimony,	trace
Sulphur	7·3	1·0	6·9
Sand,	0·6
						100·0	101·1	98·4

If an arsenide of nickel, cobalt, and iron be roasted or subjected to the joint influence of heat and air, the iron first suffers oxidation, leaving the nickel and cobalt in combination with the arsenic; so that, on the fusion of such a compound with silicious matters, after previously roasting it to a degree only sufficient to oxidize the iron, then the oxidized product (iron) is slagged off, leaving a speise of the arsenides of nickel and cobalt; while, if the roasting be again repeated upon the last-mentioned product, the cobalt first suffers oxidation, and then fusion of the imperfectly roasted materials with silicious matters yields a slag or glass of cobalt, whilst the nickel remains in combination with the arsenic. Iron, cobalt, and nickel are in descending order of oxidability, and would accordingly be slagged off in this order, as above indicated, by alternately imperfectly roasting and fusing with successive portions of silica, quartz, or other silicious matters.

158. Ores of Nickel.—Of the ores of nickel the most

important, and those from which the nickel of commerce is largely obtained, are *kupfernickel* and *nickel speise*; while the other more important of its ores are *nickeliferous pyrites*, *nickel glance*, *arsenical nickel*, etc. The ores of nickel occur in most parts of the world where other metalliferous deposits exist; but the most abundant supplies are found chiefly in Norway, Sweden, Hungary, and South America.

Kupfernickel, *false copper* or *copper nickel*, is an arsenide of nickel (NiAs_2), constituting the principal ore of the metal. It occurs as a coppery-red, opaque, brittle body, sometimes crystallised in hexagonal forms, at others in massive, reniform, columnar, or arborescent forms. Its specific gravity varies between 7.3 and 7.5, and its hardness is 5.5. Its streak is pale brownish-red; it possesses a metallic lustre, and exhibits a grey or blackish colour when tarnished. Analyses of this mineral show it to contain from 35 to 45 per cent. of nickel, the residue being chiefly arsenic, with only small proportions of sulphur, iron, etc., but occasionally antimony is present in not inconsiderable amount. This mineral occurs in Bohemia, Thuringia, Hesse, Styria, Saxony, Norway, Westphalia, Hungary, France, Cornwall, Connecticut, etc., usually associated with ores of cobalt, silver, and copper; and occurring in gneiss, mica-slate, clay-slate, quartz, syenite, etc. Other arsenides of nickel occurring native are *Cloanthite*, *Rammelsbergite*, etc.

Nickeliferous pyrites or *capillary pyrites* (NiS) is a native sulphide of nickel which occurs as a brass-yellow, brittle, opaque solid, having a metallic lustre, with a hardness of from 3 to 3.5, and often occurring in rhombohedral crystals, although most frequently occurring in strings or threads along with other minerals. It is found in Bohemia, Przibram, Andreasberg, Johanngeorgenstadt, Riechelsdorf, etc., in Cornwall, and in Pennsylvania.

Nickel glance is a silver-white or steel-grey brittle mineral, with a metallic lustre, a greyish-black streak, and a hardness of from 5 to 5.5. It occurs massive or crystallised in monometric or cubic forms. It varies much in composition, but contains usually from 25 to 30 per cent. of nickel, with from 40 to 45 per cent. of arsenic, and from 15 to 20 per cent. of sulphur; while other varieties contain from 40 to 50 per

cent. of antimony, and smaller proportions of arsenic. It occurs in Sweden, Westphalia, Thuringia, Hartz, Styria, Hungary, etc.

Amongst other minerals containing nickel in large proportions may be noted *millerite*, a native nickelous sulphide; *emerald nickel*, a native nickelous hydrocarbonate; *annabergite* or *nickel bloom* is an arseniate of nickel.

159. Extraction of Nickel.—Works for the extraction of nickel, or for the preparation of the nickeliferous regulus, speise, etc., from which the metal is extracted, exist at Swansea, Birmingham, in Belgium, Westphalia, Silesia, Saxony, Austria, Hungary, Sweden, Norway, and the United States. As already noted the metal is chiefly extracted from *kupfernickel*, or from a concentrated *nickeliferous regulus*, *speise*, etc., the latter consisting of an arsenide of nickel, etc., as indicated by the analyses on page 329, and prepared in the small works in the manner described, page 342. But besides these, other ores are treated for the production of a regulus or nickel speise; thus in the Grand Duchy of Baden there occurs a magnetic pyrites with copper pyrites, which contains from 2·5 to 5 per cent., and sometimes even 10 per cent. of nickel, and this ore is smelted in blast furnaces for a regulus which is calcined, remelted, and at last refined so as to yield a metal containing from 60 to 63 per cent. of nickel, 24 to 27 per cent. of copper, and only ·03 to ·05 per cent. of iron, which product is then sold to the nickel refiners for the extraction of the nickel. Again, in Norway the ore is a magnetic pyrites containing usually from 1·5 to 3 per cent. of nickel, although occasionally reaching to 5 or 7 per cent. of this metal. This ore is first calcined in large heaps, then smelted with coke in blast furnaces to obtain a regulus, coarse-metal, or speise, containing from 15 to 17 per cent. of nickel. This product is again roasted in kilns and smelted for a second regulus containing from 30 to 35 per cent. of nickel, which is then remelted with coke in an open hearth under the oxidizing influence of a strong blast, by which nearly the whole of the iron, with a portion of the sulphur, is oxidized, and an alloy, white metal or rich speise, containing from 50 to 60 per cent. of nickel, with from 25 to 30 per cent. of copper, and 24 to 26 per cent. of sulphur, is obtained;

and this rich speise is subsequently treated by chemical means, at the nickel refineries, for the separation of the nickel.

The exact methods of procedure observed in the extraction of nickel are kept as secret as possible; yet several methods have been published by various authors, from which the following are collected. If *kupfernickel* or *speise* be the subject of operation, the product is reduced to powder, and after sifting, it is carefully roasted at a gentle heat, for the expulsion of the greater portion of the arsenic, whilst the nickel and cobalt are oxidized; but the process requires to be repeated with an admixture of charcoal dust, so as to decompose any arseniate of nickel formed in the first roasting, and these operations are repeated until the ore ceases to evolve any arsenical vapours, or is perfectly sweet. Or instead of directly roasting the powdered speise, it is a practice at Birmingham to first fuse the speise with chalk and fluor-spar in a reverberatory furnace, then throw away the slag so obtained and grind the fused product, after which it is roasted as before in a reverberatory furnace for about 12 hours, or until arsenical fumes cease to be evolved. After this roasting the product contains principally nickel, cobalt, iron, copper, small quantities of arsenic and possibly of bismuth, and it is then subjected to a series of wet operations for the extraction of nickelous oxide free from arsenic and the other metals, and it is the exact mode of procedure observed in these operations that are generally considered as trade secrets, and not therefore usually divulged, yet, as before mentioned, numerous methods have been published, from which the following may be cited.

According to a method pursued at Birmingham, as published by Louyet, the roasted ore is to be digested with hydrochloric acid, the solution being heated by steam, when the acid thus dissolves almost the whole of the ore or regulus, and the solution so obtained contains the chlorides of nickel, cobalt, copper, iron, and possibly of bismuth, along with traces of arsenic acid; the solution is then largely diluted with water, by which bismuth, if present, is largely precipitated as oxychloride, and bleaching powder (chloride of lime) is then added to peroxidize the iron; while, should there be

an absence of iron in the solution, then ferric chloride must be added in order to precipitate the arsenic acid in the form of a basic arseniate of iron, after which the solution is neutralised by the addition of milk of lime, which precipitates as ferric oxide the residue of iron remaining in the solution. The precipitate, after well washing with water, is thrown away, and the filtrate then contains the nickel, cobalt, copper, and perhaps traces of lead and bismuth; the iron, arsenic, and most of the bismuth having been removed in the precipitate, and the copper along with any lead or bismuth remaining, are now separated by passing a current of sulphuretted hydrogen through the liquid until the filtrate gives a black precipitate on the addition of ammonia, showing that the sulphuretted hydrogen is present in excess, and that the whole of the copper has been precipitated. The solution is then filtered from the precipitate of cuprous sulphide, etc., the latter being washed with water, and the washings added to the filtrate; the solution so obtained, and which now contains only the metals, nickel and cobalt, is boiled to expel the excess of sulphuretted hydrogen, after which it is neutralised by lime, and then chloride of lime is added to precipitate any cobalt, which precipitate after ignition, is sent into the market for sale as cobaltous oxide; while the nickel is subsequently precipitated from the filtrate as hydrated oxide by the addition of milk of lime, and after washing is dried and subsequently reduced to the metallic state by strongly heating with powdered charcoal, in the manner to be subsequently described.

A method of separating the *oxide of nickel* described by Berthier, consists in first mixing the roasted speise or kupfernickel with an amount of *iron*, determined by a previous experiment as being necessary for combination with the arsenic acid, whereby the latter may be removed as ferric arseniate. The mixture of roasted materials and iron is then dissolved with the aid of heat in nitro-hydrochloric acid (*aqua regia*), containing an excess of nitric acid; this solution is then evaporated to dryness, and the product treated with water, by which much of the ferric arseniate is left as an insoluble residue, while the little that is taken up in solution is precipitated along with any cupric oxide by the addition of sodic

carbonate to the filtrate, continuing the addition of the sodic carbonate with constant stirring of the solution until the precipitate shows a green tint. The precipitate thus thrown down rapidly changes upon exposure to the atmosphere, from white to brown, and if this change does not occur, it indicates an insufficiency of ferric oxide in the solution, and it becomes necessary to add ferric chloride to the solution; whilst any excess of ferric chloride so introduced is subsequently precipitated by the cautious addition of sodic carbonate. To the filtrate is then added sulphuretted hydrogen, by which the remainder of the copper is precipitated; and the nickel and cobalt present in the filtrate are then completely precipitated at a boiling temperature by the addition of sodic carbonate. The precipitate, consisting of the carbonates of nickel and cobalt, is now thoroughly washed, and then diffused through water into which chlorine gas is passed so long as it is absorbed, after which the solution is exposed to the atmosphere for the evaporation of the excess of chlorine so introduced, and then filtered, upon which the nickel freed from cobalt passes into the filtrate as the soluble nickelous chloride, whilst the precipitate remaining on the filter consists of cobaltous oxide containing also a little oxide of nickel. The oxide of nickel is afterwards precipitated from the solution by the addition of an alkali, and when washed and dried is then reduced by charcoal.

Several other wet processes have been described for the separation of the oxides of nickel and cobalt from the roasted speise, kupfernickel, or other nickeliferous product, but the above suffice to indicate the general method pursued in the preparation of nickelous oxide from which the metal is reduced.

Metallic nickel is always extracted on the large scale from its oxide, prepared by the above or similar methods, its reduction being effected by very strongly heating the oxide with charcoal. For this purpose the dried nickelous oxide is broken up into small pieces, and mixed with powdered charcoal; this mixture being introduced into a series of fire-clay cylinders, open at their upper extremity, while their lower end is conical in form, and contains an aperture for withdrawing the charge. These cylinders are set vertically in a fire-grate

or furnace, the conical end of their lower extremities passing beneath the fire-bars, whilst their upper ends are left open for the introduction of the charge. The mixture of oxide and charcoal having been introduced, the fire is then urged strongly, when the metal reduced by the ascending current of carbonic oxide collects in the bottom of the cylinders in a very imperfectly fused state, the lumps of metal so obtained still retaining the original form of the pieces of oxide introduced, thus indicating that the reduction is effected by a species of cementation, the reduction proceeding from the exterior towards the interior without absolute fusion. The reduced metal is withdrawn at intervals through the apertures in the bottoms of the cylinders, and fresh portions of the charging mixture are added from time to time at the mouth of the cylinders, so as to render the process continuous during the whole time of the reduction, or until it is necessary to stop the process for repairs, etc. If the metal be required in ingots, it is necessary to fuse the lumps obtained in the last stage, for which purpose the strongest head of a wind furnace or forge fire is required.

160. **Alloys of Nickel.**—The chief application of nickel to the arts is in the manufacture of the various white malleable alloys, constituting *German* or *nickel silver*, *packfong*, *electrum*, and *tutenag*, formed by alloying it with varying proportions of copper and zinc; thus *German silver* is an alloy of 5 parts of copper, with from 2 to 3 parts of nickel, according to its quality and intended use, and 3·5 parts of zinc; while in *electrum*, to 8 parts of copper and 3·5 of zinc, from 4 to 6 parts of nickel are added, and the Chinese *tutenag* contains about 8 parts of copper to 3 of nickel, and 6·5 of zinc.

161. **Nickel Silver or German Silver.**—This alloy, now prepared largely as a basis for electro-plating upon, and as a substitute for silver, consists of copper, zinc, and nickel, in proportions varying with the purpose for which it is intended. The alloy, composed of 5 parts of copper with 3 of zinc and 2 of nickel, is employed for electro-plating upon; while for use in the manufacture of table-forks, spoons, etc., a better alloy, consisting of equal parts of nickel and zinc, with 2 of copper, is employed, and for rolling purposes an addition of

about 2 per cent. of lead is made; whilst for casting 50 parts of copper, 20 of zinc, and 25 of the best pulverised nickel, forms a good alloy. The addition of a small quantity of iron or steel increases the hardness and brittleness of the alloy, and at the same time renders it whiter in colour. The following analyses are given by Dr. Lamborn—

ANALYSES OF GERMAN SILVER.

	Copper.	Nickel.	Zinc.
English German Silver, : : : :	61·3	19·1	19·1
Sheffield German Silver, : : : :	57·0	24·0	13·0

Owing to the high temperature required for the fusion of the nickel, and the low melting point and ready oxidability of zinc, the preparation of this alloy is attended with a considerable loss of zinc, and special care is accordingly required in its production. In the manufacture of nickel silver, three methods are pursued: either the copper and nickel are melted together in a separate crucible, and the heated zinc added to the bath in small pieces; or the zinc is first melted with one-half of the copper, and the alloy so formed cast into thin plates so as to be easily broken, whilst the nickel is melted with the second portion of the copper in another crucible, to which, after thorough mixture, the first alloy is added in small pieces until the necessary composition has been attained; or thirdly, the constituent metals are arranged in layers in the crucible, with copper forming the lowest and uppermost layer, and the surface is then well covered with charcoal, when the crucible is heated in an air furnace with a strong draught so as to rapidly melt the metals, which are stirred continuously to ensure their thorough incorporation, especially of the difficultly fusible nickel.

German or nickel silver is greyer in colour and harder than silver, and is capable of receiving a high polish; its fracture after casting is strongly crystalline, and the alloy requires, in the first instance, careful annealing before rolling or hammering; but after the crystalline character has been thus overcome, the metal may be hammered and rolled into

a variety of forms, while some specimens possess considerable elasticity. German silver acquires a yellow tarnish when exposed to the atmosphere, and in acid solutions, as vinegar, with access of air, it becomes coated with a layer of green verdigris; heated to bright redness in the atmosphere, the alloy fuses whilst a proportion of the zinc burns away.

An alloy possessing many of the qualities of German silver may be prepared by alloying together copper and manganese, or copper, zinc, and manganese, thus substituting manganese, for nickel is the original German silver, and an alloy of this character is described at page 17.

CHAPTER VIII.

COBALT.

THIS metal is chiefly employed in the arts in the form of oxide, silicate, or other chemical combination, constituting the basis of a large number of pigments, and a material largely employed for imparting a blue colour to glass, enamels, etc. In these forms it appears to have been known from an early date, but it was not until 1733 that Brandt determined its metallic character, and succeeded in preparing the impure metal.

162. Chemical and Physical Qualities.—Cobalt is a greyish-white metal possessing a reddish tinge, and capable of receiving a high polish. It breaks with a granular or crystalline fracture, and requires a very high temperature for its fusion, though somewhat lower than is required to melt iron. Its specific gravity after fusion is 8·7; but its mean specific gravity is given by Rammelsberg as 8·957. It is strongly magnetic, although this quality may arise from the almost invariable presence of traces of nickel in the metal. It is possessed of *great tenacity*—a wire of cobalt supporting twice the weight required to break the same wire formed of iron; and Deville considers it to be the *most malleable* of the metals. Cobalt is not sensibly oxidized by exposure to air and moisture at ordinary temperatures, but it oxidizes at a red heat, and, when in a fine state of division, takes fire if strongly heated, burning with a reddish flame, and as reduced from its oxide by hydrogen it is pyrophoric. It decomposes the vapour of water at a red heat. Cobalt is slowly dissolved by the mineral acids on the application of heat, yielding thereby solutions of salts of cobalt, and if hydrochloric or sulphuric acid be the solvent employed, then hydrogen is also evolved. Cobaltous salts are pink or rose

coloured when hydrated, and blue when anhydrous, from which quality they are used as *sympathetic inks*: characters written with the solution of salts of cobalt being almost invisible, but on applying heat the salt is rendered anhydrous, and the characters appear of a blue colour. The atomic weight of cobalt is 58·7, and its chemical symbol is Co.

163. Oxides of Cobalt.—Cobalt forms two definite oxides: cobaltous oxide (Co_2O) and cobaltic oxide (Co_4O_3), and these by combination with each other, give rise to three intermediate oxides. The oxides of cobalt are the object of a regular manufacture, being employed alike by enamellers, porcelain painters, glassmakers, etc., for imparting to their wares the blue colour known as "*cobalt blue*".

Cobaltous oxide results when its hydrate or carbonate is ignited in closed vessels; and it is also produced along with cobaltic oxide, when finely-divided cobalt burns in the atmosphere. The first method yields the oxide as a greenish-grey powder, while, as prepared by the latter method, it is obtained as a blackish powder.

The *hydrate* of this oxide (cobaltous hydrate) is precipitated when potash is added to a solution of a cobaltous salt, but it loses water at $100^\circ\text{C}.$, when it is converted into the anhydrous oxide if air be excluded, or into cobaltic oxide (Co_4O_3) if exposed to the atmosphere.

Cobaltous oxide is reduced to the metallic state by hydrogen, carbon, or carbonic oxide at a red heat; and if heated with sulphur it yields sulphide of cobalt and sulphurous anhydride.

Cobaltic oxide (Co_4O_3) is a black body, produced when chlorine is passed through water holding cobaltous hydrate in suspension, or when an alkaline hypochlorite is added to a salt of cobalt.

These oxides, as already noted, are manufactured on the large scale (chiefly by the Birmingham nickel refiners) for use in the potteries and by glassmakers, enamellers, etc. In their production as commercial commodities, the regulus or *speise* obtained in the smelting of ores of nickel and cobalt, for the extraction of nickel, are first calcined; then the roasted product, containing oxides of nickel, cobalt, iron, copper, and probably bismuth, along with some arsenic in the form of

arsenic acid and basic arseniates, is dissolved in strong hydrochloric acid. The acid liquid is now neutralised with milk of lime and diluted, upon which iron, arsenic, and bismuth are precipitated, when after allowing the precipitate to settle, the supernatant liquid is drawn off into vats, made acid with hydrochloric acid, and a current of sulphuretted hydrogen is then passed through the solution, whereby copper, etc., are thrown down as sulphides, while the solution still contains the nickel and cobalt. When the precipitate has subsided, the solution is again drawn off, and the hydrated oxide of cobalt is precipitated by the addition of hypochlorite of lime or bleaching powder. The hydrated oxide so obtained, after heating to redness, constitutes the commercial "blue oxide of cobalt," or if heated to whiteness, it is known as "prepared oxide."

The impurities likely to occur in the commercial oxide are the oxides of nickel, iron, copper, lead, zinc, arsenic, antimony, bismuth, aluminum, silicon, magnesium, and calcium; it is also occasionally adulterated by the addition of chalk. If these impurities amount in the aggregate to more than 2 per cent. of the whole, the oxide is totally unsaleable in the potteries, except for exceptionally inferior purposes.

164. Phosphate of Cobalt.—This compound is precipitated as a deep violet-coloured precipitate, when a solution of sodic or potassic phosphate is added to a soluble salt of cobalt. The precipitate is used in the pigment "*Thenard's blue*."

165. Sulphides of Cobalt.—Cobalt forms compounds with sulphur, analogous to the oxides, the more important being cobaltous sulphide (Co_2S), and cobaltic sulphide (Co_4S_3). The former occurs native, but also results as a grey semi-metallic looking mass, when sulphur is projected upon the heated metal; or when cobaltous sulphate is heated to whiteness with charcoal. Cobaltic sulphide is a dark-grey body, obtained by the ignition of cobaltous oxide with sulphur and an alkali.

166. Cobalt and Arsenic.—The combinations of these elements give rise to easily fusible compounds, obtained as iron-grey, brittle products, when arsenic and cobalt are fused together. The arsenides of cobalt also occur native, consti-

tuting the chief ores of this metal, as will be indicated subsequently. The arsenides occurring native are, however, never quite pure, the cobalt being more or less replaced by nickel and iron, and accompanied by smaller quantities of other bodies.

167. Alloys of Cobalt.—With *tin*, cobalt forms a violet-coloured alloy, which is somewhat ductile. The presence of cobalt in only small quantities suffices to induce brittleness in *gold* and *silver*, and with *iron* it yields a very hard alloy. The amalgam of cobalt with mercury is silver white, and is attracted by the magnet.

168. Ores of Cobalt.—The chief ores of cobalt are the arsenides and sulpharsenides, and their commercial value depends not only upon the amount of cobalt present in the ores, but also upon their freedom from other metals, with the exception of nickel, which should be present in sufficient quantity to render its separation profitable.

Arsenical cobalt, tin-white cobalt or Smaltine (CoAs), is the most abundant ore of cobalt; it is tin-white in colour, inclining in the massive form to steel-grey. It crystallises in the regular system, has a greyish-black streak, is brittle, breaking with a granular, uneven fracture, and tarnishes by exposure to the atmosphere; before the blowpipe it emits copious arsenical fumes, and fuses but with difficulty. This ore occurs in the primitive rocks at Freiberg, Schneeberg, and Annaberg in Saxony; at Joachimsthal in Bohemia, Reichelsdorf in Hessa, and Tunaberg in Sweden; in which localities it accompanies silver, bismuth, and copper ores, it also occurs in Cornwall. This mineral always contains nickel or iron, or both, and it receives various names according as the proportions of nickel or iron are present in considerable proportion or otherwise.

A higher arsenide of cobalt (Co_2As_3), known as "*Mordumite*," also occurs native in Norway.

Cobalt glance, silver-white cobalt, or cobaltine, is a native sulpharsenide of cobalt (Co_2AsS), corresponding in composition to the analogous ore of iron, known as mispickel. Cobaltine is silver-white in colour, but possessing a reddish hue; it has a metallic lustre, is brittle, and its streak is greyish-black; it occurs crystallised in the regular or cubic

system, and also massive, granular, or compact. Before the blowpipe it emits arsenical fumes, and fuses much more readily than smaltine. This ore occurs at Tunaberg, Hokansbö, Wehma, etc., in Sweden; at Modum and Skutterud in Norway; also in Silesia, Westphalia, and some localities of Cornwall. The *smalts* of commerce are largely prepared from this ore.

Cobalt pyrites or *linnaeite* is a sulphide of cobalt, having a steel-grey or white colour, but with a yellowish tinge. It occurs in Sweden and in Prussia.

Earthy cobalt is a variety of "wad" or earthy manganese ore, but which contains cobalt.

Cobalt bloom, *erythrine*, or *cobalt mica*, is an hydrated arsenate of cobalt ($\text{Co}_3\text{AsO}_4 + 4\text{H}_2\text{O}$), which occurs of various shades of red, grey, and green, with a peach-blossom coloured streak. The earthy variety is peach-blossom colour, and is an arsenate of cobalt containing free arsenious acid. This ore occurs in compact reniform masses, or as an incrustation on other minerals, and is generally associated with lead, silver, and other cobalt ores. Cobalt bloom occurs at Schneeberg, in Thuringia, Hessia, Baden, Norway, Bohemia, Cornwall, Cumberland, and in the district of Lake Superior.

169. Extraction of Cobalt.—Cobalt is not employed in the metallic state in the arts, and its extraction is not therefore conducted on the large scale, its compounds with oxygen and silica forming the chief commercial forms in which the metal occurs. The extraction of the pure metal in the metallic state is attended with great difficulty; but it may be obtained by intensely igniting the oxalate in a covered crucible, by the reduction of its oxides with hydrogen at a red heat, or by the ignition of the oxide with charcoal. In the latter case, however, the metal is contaminated with carbon. The metal is also obtained as a fused regulus, when the mixture of cobaltous oxide and charcoal is heated in a blast furnace, the surface of the product being covered with a layer of glass, free from oxides reducible by carbon.

170. Smalt.—This is a blue pigment or glass consisting essentially of potash, oxide of cobalt, and silica, or is a silicate of potash (potash glass) coloured by oxide of cobalt; and the manufacture of this substance forms almost the only metallurgic operation in connection with cobalt ores.

The manufacture of smalts comprises two stages, first, *roasting* or *calcination* of the ores for the oxidation of the iron, etc., and the more or less perfect volatilization of their sulphur and arsenic; secondly, *fusion* of the roasted product in crucibles along with silica (in the form of powdered quartz, technically known as *sand*) and pearl-ashes (carbonate of potash), also sometimes a little nitre is added.

The ores are first carefully assorted, and the purer portions separated; when, after washing to separate the matrix and such other portions as allow of separation by these means, they are stamped, ground fine, and passed through a fine sieve. If the ore contain bismuth, it must be first subjected to a process of liquation for the separation of this metal; after which treatment, if any bismuth still remain after this process, the greater portion of it will be found forming a layer beneath the *speise* to be presently described.

The ores, thus freed as thoroughly as possible by mechanical means from gangue and foreign metals, are then *roasted*, and this forms the most important stage of the manufacture. The roasting is conducted on the bed of a reverberatory furnace, connected with flues and poison-chambers for the condensation of the large quantities of arsenious acid volatilised during the process. The charge of about 4 cwt. of the pasty ore is introduced through the front door of the furnace, and spread to a depth of 5 or 6 inches over the surface of the hearth, the latter, like the roof, being built of fire-stone, fire-brick, or tiles. The flame, along with the volatile products of the calcination, sulphurous anhydride (SO_2), and arsenious anhydride (As_2O_3), are conveyed along a flue, which returns around the fireplace before entering into the large chamber through which the products pass in their course to the stack, and where the arsenious anhydride is condensed and collected, the condensation of this product forming an important auxiliary process in the manufacture of smalts. The ore on the furnace hearth is turned over after two hours exposure, and is stirred at intervals of half an hour until the roasting has attained the desired point; the extent to which the roasting is continued depending upon the freedom of the ore from other metals, especially iron. If the ore be *free from nickel* and other foreign metals, that is, if it contains *only* arsenic and cobalt,

then it may be roasted as *sweet* as possible; when the arsenic is to a large extent sublimed as arsenious anhydride, and there remains only the oxide of cobalt, with more or less basic arsenate of cobalt, of which the arsenic acid in the latter is expelled as arsenious anhydride and oxygen, on treatment with silica at the high temperature required in the subsequent fusion. If the ore be poorer and contain *nickel* in addition, then the roasting is continued only so far as will leave sufficient arsenic in the mass, in the state of arsenide, as is required to combine with the nickel in the subsequent fusion, when the nickel will be separated as a speise, forming a distinct layer in the crucible or pot beneath the blue glass of cobalt. If, however, *both* iron and nickel be contained in the ore, it will be necessary to regulate the roasting so as to introduce sufficient oxygen to oxidize the whole of the iron present, and to leave a little more arsenic in the product in the form of arsenides than will suffice to combine with the whole of the nickel; when, on fusion, the iron, copper, and other readily oxidizable metals will pass out in the slag, while the nickel with a little cobalt will separate as arsenides constituting the *regulus* or *speise*, which forms the lowest stratum in the melting crucible; and the cobalt will be concentrated in the *smalt* or *blue glass*, forming the third product.

The above reactions depend upon the superior oxidability of iron over cobalt and nickel, and the decreasing affinity for arsenic exercised by nickel, cobalt, and iron respectively, in virtue of which cobalt may be separated from an iron slag containing it by fusing the slag with arsenide of iron, when the cobalt will separate as a cobalt speise or arsenide, while the iron passes out in the slag.

The determination of the duration of the roasting process, as also the amount of silica to be added in the subsequent fusion, is determined experimentally for each lot of ore; for which purpose a small portion of the ore is roasted and treated as in the manufacturing process, and the operation is repeated until the required tint is obtained, when the product so produced is imitated on the large scale.

The roasted ore, which is of a brownish-grey colour, and sometimes called "*safflor*," is then mixed in the proportion of about 4 parts of roasted ore to 10 parts by weight of

silica and 5 of potassic carbonate, the exact proportions differing, however, according to the tint required, and which have been previously determined experimentally. Also a quantity of the crude arsenious anhydride from the poison-chambers is added in order to neutralise the tint produced by any small quantities of iron that may be present in the product, but the exact proportion of the arsenious acid is not material, since any excess is volatilised at the temperature of the fusion. The ingredients, in quantity sufficient to supply the crucibles for one week, are mixed in long wooden troughs, the silica being employed in the form of quartz which has been heated to redness, reduced to fine powder in a stamping-mill, and then washed to free it from earthy and ferruginous matters, after which it is dried and heated to redness, when it constitutes the *sand* employed in the process. To expel moisture from the potassic carbonate (which should be free from any sodic carbonate or chloride, as also from magnesia, potassic sulphate, etc.), and to render it more easily mixable with the sand and roasted ore, it is calcined before use in a reverberatory furnace. The mixture of roasted ore, sand, and calcined potassic carbonate, is then introduced into the red-hot earthen pots or crucibles *a, a*, measuring about 2 feet in diameter at the mouth, and each holding about 80 lbs. of the mixture;

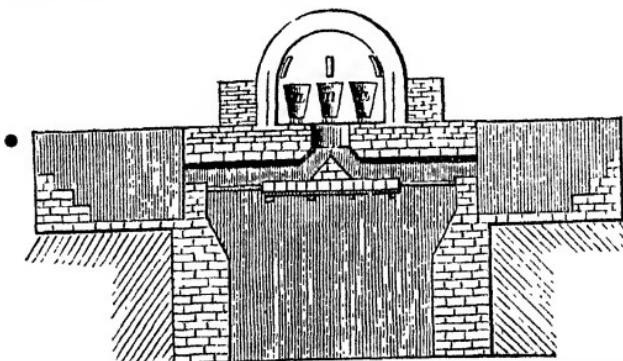


Fig. 67.—FURNACE EMPLOYED IN THE PRODUCTION OF SMALT.
and eight of these pots are arranged in a vaulted chamber or furnace, fig. 67, resembling an ordinary glass furnace, constructed so as to consume either wood or coal as fuel.

In from six to eight hours after charging the pots the fusion commences, when the workman breaks the crust that forms on the surface, and afterwards stirs the mixture from time to time. When the furnace has attained a white heat the stirring is discontinued to allow of the separation of the speise from the blue glass, and the melting is judged to be complete when the glass adheres to a rod inserted into it, and may be drawn out into fine threads. The *speise* collected in the bottom of the pot is tapped out through the aperture in the side of the crucible, and the scum from the surface is skimmed off; after which the *smalt*, *blue glass*, or *metal*, as it is called, is degraded, that is, it is ladled from the pots by a large iron ladle and poured into cold water, whereby it is disintegrated, rendered brittle, and more easily reduced to powder; and, when all the pots are emptied, recharging commences.

If nickel be present in the cobaltiferous ores, there is produced in the crucibles *speise*, *blue glass*, and *glass gall*, each forming a distinct layer, the *glass gall* constituting the uppermost stratum or scum; the *blue glass* constitutes the middle layer, and lowermost occurs the *speise*. The *speise* is a semi-metallic looking body, which is subsequently used for the extraction of nickel; it has a variable composition, but is essentially an arsenide of nickel, containing also small quantities of other metals, as indicated by the accompanying analyses—

ANALYSES OF SPEISE.

ANALYST,.....	Berthier.	Will.
Nickel,	49·0	52·6
Arsenic,	37·8	40·5
Iron,	2·7
Copper,	1·6	1·6
Manganese,
Cobalt,
Antimony,	3·2	trace
Sulphur,	trace 7·8	... 2·5
	99·4	99·9

The smalt thus disintegrated by pouring it into cold water, is then stamped or crushed between rollers, after which it is ground to a very fine powder or impalpable pulp between a pair of granite stones, working beneath the surface of water contained in a wooden trough. After some hours grinding, the contents of the trough are drawn out into tanks, where the purest and darkest coloured smalt quickly subsides to the bottom, when the water, still holding in suspension a considerable proportion of solid matters, is drawn off into a second series of troughs, where a less pure product is allowed to subside; while the operation of letting out and again allowing to settle is repeated for the separation of still inferior qualities of the product, the time allowed for subsidence in each trough increasing in each from the first; thus a few minutes will suffice for the separation of the first quality, while about an hour is allowed for the second subsidence, and so on. Instead of drawing off the water from each tank in the manner just described, the process may be conducted by grinding the blue glass in a tank through which a gentle stream of water is continually flowing, when the water, carrying the smalt in suspension, is made to pass through a series of depositing vessels or tanks, so arranged that the overflow from the one passes to the next below it in the series, and each one is made larger than its predecessor, so as to hold the water for a longer time, as required for the separation of the finer particles with which the water is charged as it gets further away from the grinding apparatus; while the colour of the product at the same time diminishes in intensity in each tank from the first to the lowest of the series. The different qualities of the product thus obtained are each again subjected to a further levigation, and for this purpose the smalt is broken up, introduced into troughs, and thoroughly agitated by the workmen, when, after a few minutes of rest, the water holding in suspension the finer particles of smalt, with the impurities, glass gall, etc., is run out into other troughs for further subsidence, and so on with each quality; this breaking up and washing being repeated several times upon each quality of the product, with the allowance, after each washing, of a longer period for the subsidence, the time extending to 20 or 24 hours in the last stage of the washing operations.

The various qualities of the product thus thoroughly washed, after drying, which may be performed either in stoves or by atmospheric influence, are ground to a fine meal between rollers or other appliances, and is then carefully sifted through a fine hair sieve, and the smalt or azure is then ready for the market.

Various other more purely chemical methods have been adopted at different works for the preparation of smalt, according to which processes, the ore, after careful roasting, is treated with sulphuric acid, or fused with potassic sulphate; when the sulphates produced by either method are treated with water, after which potassic carbonate is added to the solution, whereby the iron is first precipitated and removed, when, if the addition of potassic carbonate were repeated, the cobalt would be precipitated as cobaltous carbonate, which could be used for the production of smalts by fusion with silica, etc.; or, in another modification, the potassic carbonate is added to the solution of the mixed sulphates, only until the cobalt begins to be precipitated, as evidenced by the colour of the precipitate, when the liquid containing cobalt in solution is decanted, and a solution of a soluble silicate of potash added to it, by which a silicate of cobalt is precipitated that may be used for painting purposes. These methods are practised in Prussia and in Sweden.

Cobalt glass or *smalt* is, as previously noted, essentially a mixture of different silicates, which are, however, referable to two classes: the one containing an excess of potash is soluble in water, while the other contains an excess of basic silicate of cobalt, and is insoluble in water; and this difference in solubility may possibly account for the different tints produced in the series of levigations to which it is subjected.

The various qualities of the smalt or azure, obtained by the series of levigations above described, are marked in commerce, commencing with the highest quality, FFFFC, FFFC, FFC, FC, C and O, respectively; whilst other products from the process, and which are employed for the production of grey tints, also receive in the trade special marks indicating their quality.

The value of the smalt depends upon its purity of colour, and it hence becomes necessary that great care be exercised

in the selection of the materials to be employed, since a pure tint is never obtained from ores containing large quantities of other metals, traces of which find their way into the smalt with a corresponding deterioration of the colour; and hence pure ores are in request for this manufacture. Sodic carbonate cannot be substituted for the potash salt without loss of purity and lustre of the colour; lime, magnesia, and alumina, if introduced with the charge, have a similar effect; and small quantities of copper or nickel impair its quality, the former imparting a red or green tint to the smalt, while the latter gives a violet tint to the product, and the presence of zinc has likewise the effect of giving a greenish tint to the product.

The *adulterations* or *impurities* most likely to be found in commercial smalts are: oxides of nickel, iron, copper, zinc, arsenic, lead, antimony, bismuth, magnesium, calcium, aluminium, and silicon, with sometimes also an addition of chalk (calcic carbonate).

Smalt or *azure* is used for painting and colouring glass, porcelain, pottery, and earthenware, though for this latter a mixture described below, and known as "*zaffre*," is largely employed. Smalt is also employed to neutralise the yellow tint of paper by the paper manufacturer, and for a similar purpose by the bleacher in finishing linen and fine cotton goods.

171. Zaffre or Sapphire.—These terms are sometimes used as synonymous with smalt, but they are commercially applied to a distinct product. Zaffre is a mixture of roasted cobalt ores along with silica (flint powder) in sufficient quantity to yield, when fused with potassic carbonate to the amount of one-fourth of the weight of ore and sand together, a smalt of the desired tint. As in the production of smalt, the necessary amount of silica to be added to the roasted ore for the production of the desired tint, when fused with the constant amount of potassic carbonate, is determined by a previous experiment, or repetition of the process on a small scale.

The substance known in the potteries as "*Printer's blue*," and used for painting or printing the ordinary blue colour upon pottery-ware, china, etc., is formed by fritting, that is, heating to a point below perfect fusion, a mixture of silica and oxide of cobalt in proper proportions, along with a little nitre and a little baric sulphate (BaSO_4).

172. Thenard's Blue.—This pigment is a compound of *oxides of cobalt* and *alumina*, prepared by adding to a solution of a cobaltous salt, a solution of hydro-dipotassic phosphate, and precipitating thereby a cobaltic phosphate, when to 2 parts of this precipitate are added 16 parts of the gelatinous alumina precipitated by the addition of sodic carbonate to a solution of alum. The ingredients are well mixed, dried, and ignited at a dull red heat, in covered crucibles, any access of the products of combustion to the contents of the crucibles being avoided as carefully as possible, since the reducing action exercised by these gases materially impairs the colour of the product. To further prevent the action of the gases upon the product, an addition of mercuric oxide is frequently made to the charge, whereby an atmosphere of oxygen is maintained in the crucible, while the mercury is entirely volatilised; or 1 part of arsenate of cobalt is added in lieu of the latter, in the preparation of this pigment. The product, or Thenard's blue, is used largely for printing on pottery-ware.

173. Rinman's Green.—This is another cobalt pigment known also as *cobalt green*, and is a mixture of cobaltic and zincic oxides. It is prepared by precipitating a mixed solution of zincic and cobaltous sulphate with sodic carbonate, and igniting in a porcelain crucible, the well-washed precipitate so obtained; or a solution of cobaltous nitrate, mixed with zincic oxide (ZnO) or zincic nitrate, yields, on evaporation and subsequent ignition, the same product.

CHAPTER IX.

ALUMINIUM.

174. **Physical and Chemical Qualities.**—Aluminium is a white metal tinged with blue, and whose surface is capable of receiving a high polish. It is very malleable and ductile, permitting of being hammered into thin sheets and drawn into fine wire, though in these operations, and especially the latter, it becomes brittle, and requires frequent annealing. It is about equal to silver in tenacity and elasticity, and is highly sonorous. It is a very light metal, its specific gravity ranging from 2.5 to 2.7 only, according to its previous mechanical treatment, and this quality has led to its application for the manufacture of very small weights, etc. Its melting point is above that of zinc, but below that of silver, and it may be readily cast after fusion in metallic or sand moulds; while if cooled slowly after fusion, it exhibits a crystalline structure upon fracture. Pure aluminium is not acted upon by exposure to the atmosphere at ordinary temperatures, and this quality, together with its white colour and the facility with which it may be polished, have led to its introduction for the purposes of jewellery, the mountings of philosophical instruments, etc. It slowly decomposes steam at a red heat; it is unacted upon by sulphuretted hydrogen or ammonium sulphide, thus preserving its lustre unimpaired in atmospheres contaminated with these gases, and it only combines with sulphur when heated along with it to a very high temperature. Aluminium does not exhibit any tendency to volatilise when heated in closed vessels. It is a very good conductor of both heat and electricity, in which respect it ranks about equal to silver.

Aluminium is not acted upon by dilute or concentrated cold nitric acid, and only slowly by the boiling acid; neither is it affected by dilute sulphuric acid, while the vegetable acids, as

acetic and tartaric acid, are also without sensible action upon it; but hydrochloric acid forms its best solvent, readily dissolving the metal accompanied by the evolution of hydrogen. Potassic or sodic hydrates in a state of fusion do not attack the metal, although their solutions dissolve it readily with the evolution of hydrogen and formation of potassic or sodic aluminates respectively. It may be fused with nitre at a moderate heat without undergoing oxidation; but at a temperature sufficient to decompose the nitric acid and evolve nitrogen, then the metal is attacked, and a potassic aluminate is again formed. The chemical symbol of aluminium is *Al*, and its atomic weight is 27.5.

175. Oxide of Aluminium.—Alumina, or the sesquioxide of aluminium (Al_2O_3), constitutes the only known oxide of aluminium; and this occurs almost pure in the gems *sapphire*, *ruby*, *oriental topaz*, and the *oriental amethyst*, the two former owing their colour to the presence of a little chromic oxide; while as a more impure native product, it constitutes the brownish red variety of corundum known as *emery*, and thus in its native forms it occurs as one of the hardest substances known.

Alumina can be prepared artificially by heating the finely-divided metal in air or oxygen, when this oxide results, although in the massive form, the metal, as already noted, is not oxidized even at a much higher temperature. Other and more convenient methods, though not affording an absolutely pure product, consist in igniting ammonia alum (the double sulphate of aluminium and ammonium), when this oxide remains; or boiling a solution of common alum with ammonic carbonate, washing with water the precipitate so obtained, and afterwards igniting it to expel the combined water; or alumina may be prepared from clays, felspathic rocks, cryolite, etc., by digesting these with potash or soda, so as to produce an alkaline aluminate, which is then decomposed by carbonic acid.

Artificially prepared alumina is a white body, which is infusible except in the oxyhydrogen flame. When the heat employed in its preparation has not exceeded redness, it forms a very light and soft powder, but after strongly igniting, it becomes intensely hard and gritty. The anhydrous oxide is insoluble in water, and after strong ignition is likewise

insoluble in most mineral acids, except concentrated hydrochloric or sulphuric acid, which effect its solution.

Alumina forms three hydrates, of which the trihydrate falls as a white gelatinous precipitate when ammonia or an alkaline carbonate is added to a solution of alum, etc., in which form the hydrate is readily soluble in acids. From the strong affinity of this compound for organic colouring matters, it is extensively employed as a *mordant* in calico printing and dyeing, as also in the preparation of the pigments known as *lakes*.

176. Aluminic Silicates.—The silicates of alumina constitute a very large and important class of natural and artificial products. Thus silicate of aluminium forms the basis of all *clays*, while the individual and special character of the clay depends chiefly upon the nature and amount of the foreign matters present, and of the other silicates often associated with the silicate of aluminium in its composition; thus *kaolin*, *porcelain* or *china-clay*, from which the finer kinds of porcelain are manufactured, is almost a pure hydrated aluminic silicate, whose composition is approximately represented by the formula $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 + 2\text{H}_2\text{O}$; *Potter's clay*, used in the production of the coarser kinds of earthenware, contains in addition about 7 per cent. of iron, and 2 per cent. of lime. The *blue clays* are frequently coloured by organic matters, which on ignition are burnt out, and the burnt clay becomes white, or of a reddish tint if also containing iron. The various *fire-clays* are also hydrated silicates of alumina,* owing their plastic property to their combined water.

Silicates of aluminium, in combination with potassic and sodic silicates, constitute the varieties of *feldspathic* rocks, which, by their disintegration and decomposition under atmospheric influences, etc., yield the various clays.

Besides constituting the bulk of certain rock masses and clays, these silicates also occur under slightly different forms in a large series of minerals, each receiving specific names, but whose consideration constitutes the province of mineralogy.

177. Occurrence of Aluminium.—This metal occurs in a great variety of forms, and its combinations altogether constitute it one of the most widely distributed elements upon

* Vol. I., page 15.

the earth's crust; in the form of oxide (alumina) it occurs anhydrous and hydrated, often associated with ferric oxide constituting *bauxite*, with magnesic oxide as *spinelle*, and also with zincic and other oxides; while as silicate it constitutes, as above noted, the base of all clays and soils; and in combination with fluorine, as a double fluoride of aluminium and sodium, it occurs as "cryolite" ($3\text{NaF}, \text{Al}_2\text{F}_8$), the mineral from which the metal is largely obtained commercially.

178. Preparation of Aluminium.—This metal was formerly obtained by the decomposition of aluminic chloride by means of potassium, and it is still the practice to effect the decomposition of the aluminium compound by potassium or sodium, but preferably by the latter, since it is considerably cheaper and less violent in its action, whilst its lower atomic weight enables it to decompose a larger quantity of the compound of aluminium than is effected by the same weight of potassium. The method of preparation still pursued is the same in principle as that employed by Wohler in 1828, when he succeeded in separating the metal as a grey powder intermixed with globules of metal, by igniting the chloride or fluoride of aluminium with sodium.

Saint-Claire Deville and others have since, however, succeeded in preparing the metal in much larger quantities. The method first employed by Deville consisted in passing the vapour of aluminic chloride (Al_2Cl_6) over metallic sodium maintained at a red heat in a copper or iron tube suitably arranged. In this manner the metal was separated and remained in the tube, mixed with sodic chloride and undecomposed aluminic chloride, these latter compounds being then dissolved out by washing with hot water; or the product was again fused in an atmosphere of hydrogen, and subsequently refused in a crucible, when the metal largely subsided as a button beneath the layer of the mixed chlorides.

On the large scale the decomposition is effected upon the bed of a reverberatory furnace, in which case the metal is reduced either from a double chloride of aluminium and sodium prepared from the mineral "bauxite," or directly from the mineral "cryolite" (a double fluoride of aluminum and sodium). In the former case the bauxite is first employed for the preparation of gelatinous alumina, which product is then mixed

with sodic chloride and charcoal, formed into balls, and introduced into earthen retorts, where they are now heated to redness, while a current of chlorine is passed through the apparatus, when the volatile double chloride of aluminium and sodium distils over. In the manufactory of Messrs. Bell* of Newcastle, 10 parts of the double chloride so obtained is mixed with 5 parts of cryolite or fluor-spar, both in a state of fine powder, and to this mixture is then added 2 parts of sodium in small ingots or pieces, each piece being well dried and freed from naptha before using. The whole is now introduced on to the hearth of a reverberatory furnace previously heated to the required degree, when a violent reaction ensues, during which the dampers are closed, and all parts of the furnace kept as close as possible to prevent access of air; the whole mass is thus almost completely fused, and when the action subsides and the decomposition is completed, the furnace is tapped, and the metal with its accompanying slag is received in proper moulds; where the aluminium collects largely in the bottom, above which occurs two strata of slag, the uppermost consisting largely of sodic chloride, beneath which is the second layer, less fusible than the uppermost, and consisting for the most part of fluoride of aluminium, in which is mechanically held a further proportion of the reduced metal, which is recovered by pulverization and sifting of the slag. This process has been patented in France and England by M. M. Rousseau Frères, and M. Paul Morin.

A less pure quality of aluminium, contaminated with silicon or iron according as earthen or iron crucibles are employed in its preparation, is obtained by the direct decomposition of the mineral cryolite ($3\text{NaF}, \text{Al}_2\text{F}_3$) as originally practised by H. Rose in Berlin, and by Dr. Percy and Mr. A. Dick in England, is still pursued in France, which process possesses the advantage of avoiding the necessity of the preliminary and troublesome process necessary for the preparation of the double chloride of aluminium and sodium required in the previous process. For this treatment the cryolite is finely powdered and mixed with half of its weight of sodic chloride, and the mixture is then introduced into earthen or iron crucibles in alternate layers with the sodium, 2 parts of

* Makin. *Metallurgy.*

sodium being introduced to 5 parts of cryolite, a layer of cryolite forming the top layer, when the whole is covered with a layer of sodic chloride. The crucible and contents are now rapidly heated, under which treatment the mixture enters into fusion, when the charge is well stirred with an iron rod and then left to cool. Upon breaking the crucible the aluminium usually occurs in large globules, which are subsequently remelted for casting into ingots.

179. Alloys of Aluminium.—Aluminium readily alloys with most of the metals, it thus unites with *zinc* and *tin*, yielding brittle alloys, and with *iron* also it unites in all proportions, affording hard and brittle alloys of no practical application to the arts. With *silver*, aluminium may also be alloyed, but the metal loses thereby in malleability, while when containing only 3 per cent. of silver, the resulting alloy has the colour of silver, and is not tarnished by sulphuretted hydrogen; yet of the several alloys of aluminium, the most important are its combinations with *copper*, producing thereby the commercial alloy known as "*aluminium bronze*."

Aluminium bronze is an alloy of copper with from 3 to 10 per cent. of aluminium, and is in many respects an important and remarkable body. The alloy containing from 3 to 5 per cent. of aluminium has a yellow colour almost like gold, it is hard though malleable, and is capable of receiving a high polish. With 10 per cent. of aluminium, its colour is more like brass, and specimens of this composition have been tested by Dr. J. Anderson, C.E., and found to possess a tensile strength of 43 tons to the square inch, but this remarkable tenacity is not possessed by all specimens, and the very wide differences thus afforded by similar alloys have prevented its introduction as a constructive material, and the chief applications of this alloy have accordingly been for the production of ornamental articles. Aluminium bronze may be prepared by heating a mixture of alumina and oxide of copper* with charcoal; or a mixture of alumina and charcoal with granulated copper may be substituted, maintaining the charcoal in all cases slightly in excess of that required for atomic proportions.

* Watts' *Dictionary of Chemistry*.

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